DEVELOPMENT OF A METHODOLOGY BASED ON ODD RANDOM PHASE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TO EVALUATE CORROSION PROTECTION OF COATINGS

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ABSTRACT

Commonly coatings are used to protect metals from corrosion. Different types of coatings are available and according to their characteristics they provide different levels of protection.

In order to evaluate the performance of the coating, it is fundamental to have a methodology that is reliable and efficient even when applied to different kinds of systems.

A good candidate technique to develop this methodology is the Electrochemical Impedance Spectroscopy (EIS). Among the advantages provided by this technique there are the ability to detect corrosion and the fact that the measurements are non-destructive. Recently Odd Random Phase Impedance (ORP-EIS) was developed. In comparison to classic Impedance, it allows for a reduction of measurement time by gathering information over a broad frequency range with a single measurement. In addition to that it is also possible to have direct information about the steady-state condition of the system by evaluating the recorded noise levels.

The methodology consists in the use of ORP-EIS combined with aging procedures. It is applied to different organic coated systems with different characteristics, including self-healing ones. Part of the coatings are applied on the same type of substrate, hot dipped galvanized (HDG) steel, in order to isolate the information uniquely linked with the protective layer.

1. INTRODUCTION

The use of organic coatings is one of the most common and cost effective choices for corrosion protection of metals [1].

In order to evaluate the protection properties of coatings, there is the need to evaluate their behavior under weatherable conditions. The most appropriate test is field exposure, which on the other hand is time consuming. To limit this problem several accelerated ageing methods have been developed over the years. One of the most commonly used in the industry is the ASTM B-117 or salt spray test. Unfortunately this method is not able to reproduce the real failure mechanism that will occur during field exposure and on top of that also usually the evaluation of the corrosion is made by a trained observer.
In order to have an early stage detection of corrosion Electrochemical Impedance Spectroscopy became a handy tool. The advantages of this method are numerous. In particular it is non-destructive and it has the capability to detect ongoing corrosion already at an early stage. The downside of the technique is that it requires experts with some experience in coating evaluation to be able to model and evaluate the coating in a limited amount of time.

2. MATERIALS

In order to evaluate the capability of the methodology to be applied to different types of coatings, different type of materials were investigated. Regarding the substrates, two different kinds were used in two different phases of the research. Initially an aluminum substrate was used and afterwards a hot dipped galvanized steel substrate was introduced. On the aluminum (rolled sheet with purity 99.99%) a shape-memory segmented polyester-polyurethane block copolymer was applied. This was produced at the VUB according to the work of D’Hollander [2]. On the other hand on the HDG steel only commercially available epoxy based coatings were applied. All the coatings were applied using the bar coating method. The thickness of the coatings varies according to the material applied.

3. METHODS

During this work the attention is concentrated to one specific technique for the evaluation of the coating, Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) [3]. ORP-EIS is a technique that has all the traditional advantages of EIS with several specific additional features. The main advantage is the capability to screen corrosion using the recorded noise levels. Through this noise it is possible to visualize both non-linear and non-stationary behavior. This allows the user to have immediate easy to detect information about the on-going corrosion processes. This information combined with the traditional evaluation of the impedance values becomes a very powerful tool. In fact, the noise levels are not only used as direct information about the system but they can also be used to optimize the equivalent circuit model used for the fitting of the system. In addition to this, ORP-EIS also reduces sensibly the acquisition time of the impedance. In fact the ORP-EIS technique is based on multisines. The ability of reducing the acquisition time is due to the fact that instead of recording the impedance value linked with each applied frequency one at the time, the multisine technique is able to apply all the set of frequencies chosen at the same time and record the associated values simultaneously. To evaluate the barrier properties of the coatings both ageing techniques (traditional methods such UV exposure) and induction of defects (scratches) were used.

4. RESULTS

So far it was possible to prove how ORP-EIS is capable of being a handy tool for several different aspects in evaluating and even choosing an appropriate new coating.
In fact from figure 1 it is possible to see how among different produced self-healing coatings with different content in polyurethane concentrations one of them had the better performance as can be deducted from their noise levels.

![Figure 1: ORP-EIS performed on different self-healing coatings after 24h of immersion in Na$_2$SO$_4$.](image1)

![Figure 2: Prove of the complete recovery of the barrier properties of the SH coating.](image2)

In figure 2 on the other hand, using just the information about the impedance values it was possible to prove the full recovery of the barrier properties of the chosen SH coating after the application of a defect, in this case a scratch. On this sample an accelerated ageing test such as the ASTM B-117 was not performed, because the polycaprolactone (PCL) is biodegradable and thus it would not withstand the high humidity content of the atmosphere.

Regarding the other coatings applied on HDG steel, the accelerated ageing experiments are still on-going. However it is possible to present here the recorded ORP-EIS graphs linked with the coating as deposited.

Looking at figure 3 it is possible to evaluate the protection ability of the coating while in figure 4 the impedance linked with the coating after 1 week ageing in a climate chamber is presented.
5. CONCLUSIONS

Even if the ageing of the traditional coatings applied on HDG steel is still on-going, definitely we can say that the ORP-EIS can be applied successfully in the development of a methodology that can be used both for traditional coatings and self-healing ones.

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REFERENCES