

Electrochemical Studies of Weldable Thin Primers

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Introduction

Conductive primers are of major importance to the automotive industry due to their weldability properties, which allow their application as coil-coating and later use in forming and assembling operations. The metal particles in the coating are in principle protected by the organic phase and therefore should resist attack by the environment, but forming operations leave some of these particles exposed, and sometimes also the underlying substrate. Weldability can be ensured by using conductive primers in the formulation, namely graphite, zinc or zinc alloys. These primers are usually very thin, below 5 μm , and the particles play a crucial role in their machinability. Since galvanized steel is used as substrate in the automotive industry, the role of the metal particles is not aimed at sacrificial protection, but rather the conduction across the coating. Zinc is added to the formulation in its metal form, as a powder, although with low metal content compared to the classical zinc-rich primers for steel substrates.

Compared to pure zinc, some alloys constitute an interesting alternative to zinc-rich primers. In particular, the Zn-55%Al alloy benefits from the passive behaviour of aluminium and thus seems to improve corrosion resistance [1,2]. Although much has been published in the past twenty years on the study of barrier coatings by electrochemical techniques [3], little is known on the electrochemical properties of thin conductive coatings. The work now reported deals with galvanized steel substrates coated with a Zn-55%Al-based organic primer versus corrosion protection and addresses the question of the electrochemical properties of these coatings, particularly in terms of Electrochemical Impedance Spectroscopy (EIS) and the Scanning Vibrating Electrode Technique (SVET).

Experimental

The substrate consisted of electro-galvanised steel with a nominal zinc thickness of 7.5 μm , onto which a 3.5 μm an epoxy matrix with ~45% of dispersed Zn-55%Al microscopic particles was applied. The film was applied by means of a lab-scale coil coating process and subsequently the primed material was formed by biaxial strain with elongations of 6%, 15% and 33%.

SVET measurements were performed using Applicable Electronics Inc. equipment controlled by the ASET software (Science Wares, USA). Impedance measurements (Gamry PC4, Gamry Instruments, USA) were made with the samples exposed to 0.05 M NaCl aqueous solution, using a three-electrode arrangement.

Results and Discussion

The SVET technique has revealed quite sensitive to the local currents, although information on the electrode size and geometry could not be obtained. These anodes and cathodes are most likely associated with particles, either electrically connected to the substrate or to neighbour particles, or just undergoing self-corrosion, as a metal island at the top of the polymer matrix. With time, these anodes and cathodes shifted from place to place on the surface, always with low current densities for the duration of the experiment. The current distribution results from the plastic properties of the coating: high deformation exposes the substrate, forming a galvanic couple and thus accelerating oxidation, whereas low deformation only exposes a larger area of the pigment.

Mapping of the ionic currents in solution has shown distinctive patterns of the formed and the non-formed samples, based upon the lifetime of anodes and cathodes at the surface. A good correlation between the SEM inspection of the surface and the SVET maps was observed.

An equivalent circuit was proposed impedance response of the system, in which the active metal is described by three relaxation processes, for the active particles directly exposed to the solution, for the polymer layer and also for the metal particles embedded in the coating, which only become active once the solution penetrates the polymer. It was concluded that the SVET and the EIS techniques give complementary information on the effect of microdefects generated on weldable primers by the forming operations.

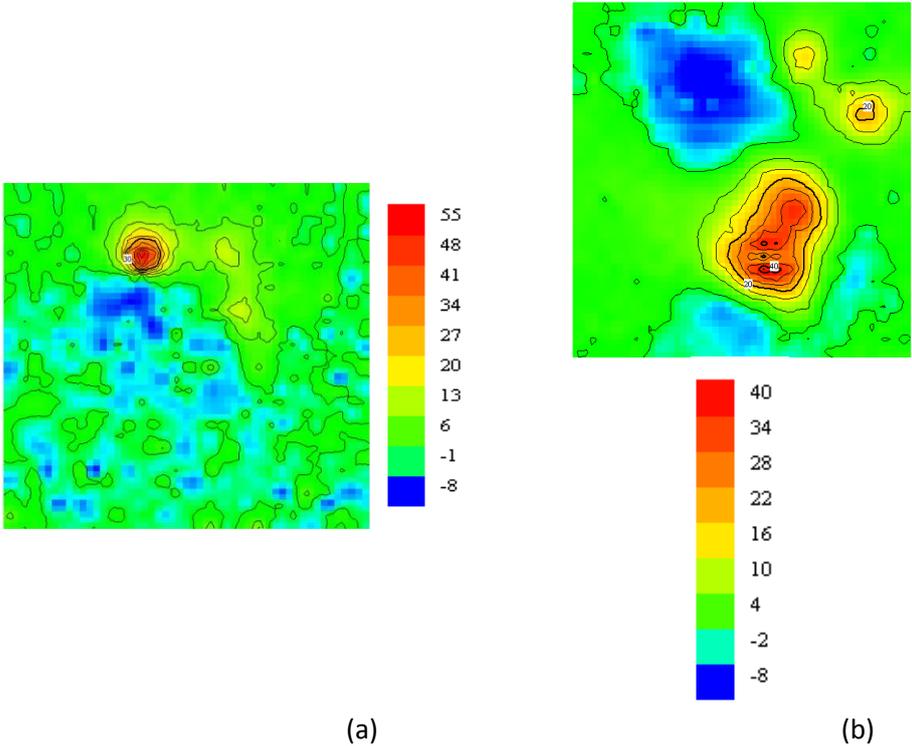


Figure 1- Ionic current maps for coated electrogalvanized steel with biaxial deformation of 6% (a) and 33% (b); scanned area: 2 mm* 2mm; scale: $\mu\text{A cm}^{-2}$. Obtained after 1 hour immersion.

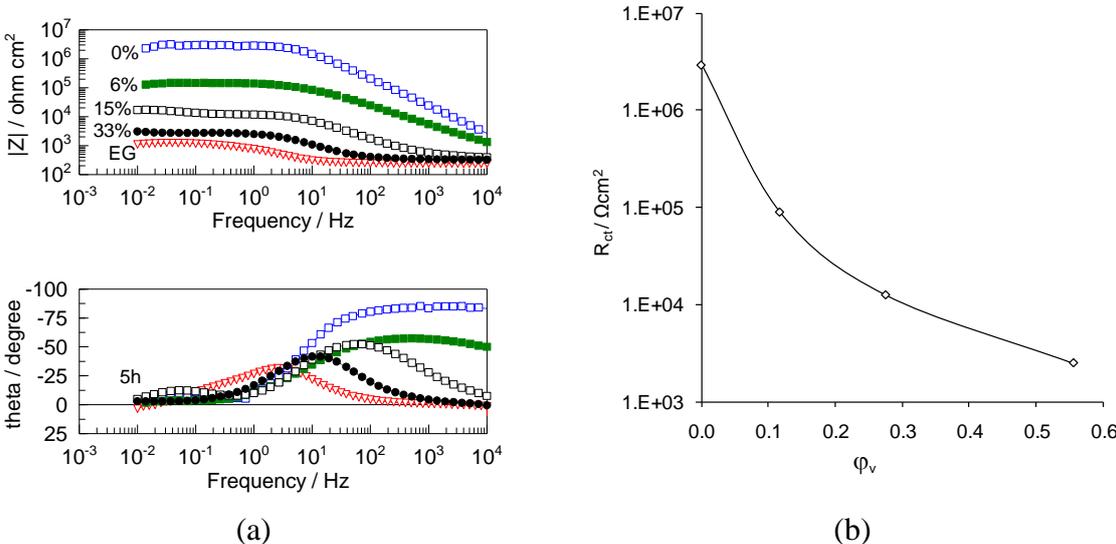


Figure 2-. EIS spectra of the strained samples (a) and effect of strain on the charge transfer resistance (b).

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References

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