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EIS and SVET assessment of corrosion resistance of thin Zn-55% Al-rich primers: Effect of immersion and of controlled deformation

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ABSTRACT

The effect of biaxial strain on the electrochemical behaviour of a thin weldable primer containing zinc-aluminium particles applied to galvanized steel was studied by assessing both the integral behavior of the system and the micro-currents on the heterogeneous surface. The ionic currents near the surface were measured by the SVET and revealed to be sensitive to the shape and lifetime of micro-active areas of the coating. The EIS data on intact coatings revealed that immersion time caused a drop of the low frequency resistance while the capacitive slope remained constant; on elongated samples, a similar trend in low frequency was observed along with an increase of the capacitance. A model is proposed, based upon an electrical equivalent electric circuit that includes distinct elements mimicking the electrochemical behaviour of the exposed and embedded metal particles and for the polymer phase.

1. Introduction

In the past twenty years automotive manufacturers, have definitely moved from plain steel to galvanized steel as the main material for car bodies. Zinc protects steel from corrosion by sacrificial anodic dissolution but also by the formation of a stable layer of zinc corrosion products that causes moderate inhibition of the cathodic reaction. Zinc-rich primers (ZRPs) are also based upon this principle. One more recent application of zinc additives to organic coatings concerns weldable primers. Weldable primers are organic coatings that are applied to metal substrates to protect them from early corrosion but which are due to allow subsequent spot-welding and cataphoretic painting [1,2]. Unlike the classical ZRPs, the main role of the zinc-aluminium particles is the conduction across the coating for weldability enhancement without compromising the life of the welding electrodes [2–7]. Conductive particles are added to the formulation with much lower content when compared to the ZRPs [8–15]. Industrially, the coated sheet composed of the steel substrate with the zinc layer and the weldable primer is cut, formed and finally spot-welded to the other body parts. During this process, forming operations are a major issue regarding the performance of the coating and ultimately the durability of the vehicle, due to the risk of formation of micro-cracks that later may act as preferential sites for corrosion initiation [16]. The correlation between deformation and corrosion performance is thus a matter of relevance for automotive manufacturers as the barrier properties can be significantly affected [17]. Electrochemical Impedance Spectroscopy (EIS) is probably the fastest method for assessing the corrosion resistance of painted metals, as it allows ranking of different coating systems in just a few days or even hours, while accelerated and field-exposure tests may require months or even years to be completed.

Modelling of organic barrier coatings is usually made using the classical equivalent circuit proposed by Haruyama [18], which associates the coating properties with a high frequency capacitive loop, while delamination is revealed by the development of a second relaxation constant at lower frequencies [5]. Haruyama's model has been applied to painted systems with barrier coatings under increasing elongation [19–21] and it was concluded that the impedance decreased with the penetration of water and of ions from the outer medium and also with the loss of barrier properties. Water absorption models have been proposed by Brasher [22] and also by other authors [23,24], including our own research group [25]. These models use either the variations of the coating capacitance associated with a growth of the dielectric constant, or the frequency distribution of the pseudo-capacitance, described as a constant-phase element [26]. In formed samples the corrosion process starts earlier and occurs at a higher rate, but also the capacitance of the coating tends to increase with strain [16,27]. In a systematic study using different kinds of strain, an improved correlation with the low frequency impedance in a barrier coating has been obtained when the equivalent strain was used [19]. Further, the use of cells that allowed the measurement at small areas along the surface, has allowed computing of the overall

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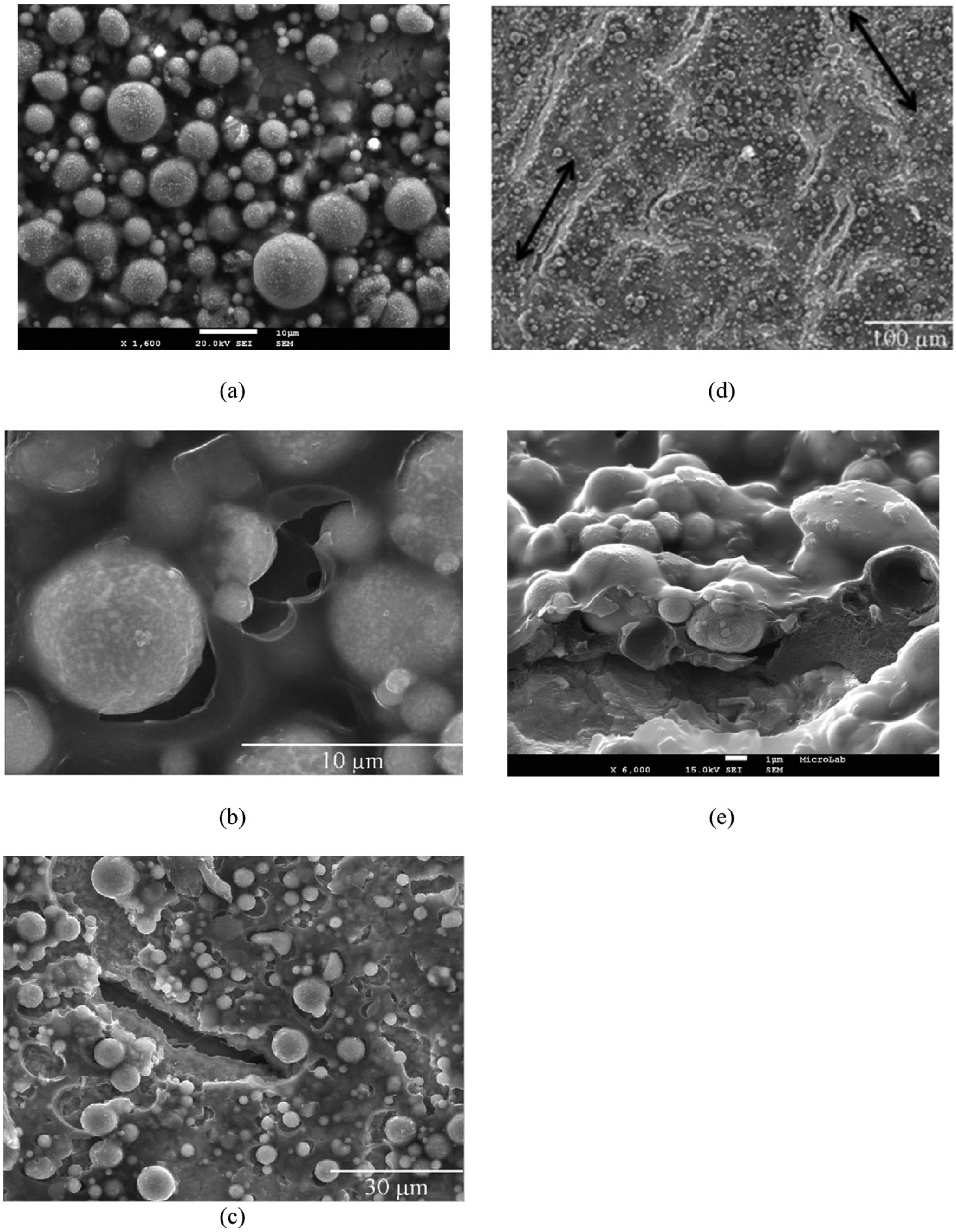

Fig. 1. Micrograph of the primed samples, (a) as-received and after biaxial strain with elongation of (b) 6%, (c) 15%, (d) 33% and (e) fractured area of as-received sample.

impedance response based upon local results and partial equivalent electrical circuits [28].

EIS studies on coatings containing zinc and/or carbon particles have been reported by some authors. According to Abreu et al. [29], Touzain et al. [30] and Vilche et al. [11], the classical Randles-type circuit cannot adequately describe metal-rich primers, as it does not explain the formation of a third capacitive loop after long exposure times. Modelling using a transmission line has been applied, considering the contact impedance between several zinc particles embedded in a porous polymer matrix. In the case of two capacitive loops, the contact impedance is measured at high frequencies while the low frequency response is attributed to a Warburg-type diffusion process related to growing of corrosion products inside-out the porous coating [9,29,31]. A third time constant is due to the corrosion process at the surface of the embedded particles. For a low porosity coating containing zinc particles, Meroufel [32] observed initially a single capacitive loop and proposed a model consisting of two mixed time constants corresponding to binder properties and the contact impedance, whereas a second loop, corresponding to the Faradaic response of the embedded particles became visible only after several days of immersion [30]. Simple circuits, with two or three time constants, including or not Warburg diffusion, were used by Klüppel et al. [17] and Bastos et al. [2], who studied zinc-rich weldable primers comparable to our own system. In a recent work, Gergely [33] proposed also this kind of equivalent circuits for primers with zinc and carbon nanotubes, but only after long immersion times, suggesting that conduction across the particles becomes significant after absorption of electrolyte and consequent wetting of the particles. Akbarinezhad [34] studied a primer containing