

Electroless Ni-P\alginate microgels coatings with self-healing properties

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Abstract

Self-healing coatings, offering corrosion protection on an alloy steel substrate, were fabricated by electroless co-deposition of a Ni-P matrix together with alginate microgels incorporating nickel salts and sodium hypophosphite. Reconstruction of the metallic coating occurs whilst it is immersed in 3.5% NaCl solution, due to the autocatalytic reaction of nickel deposition.

Keywords

self-healing coating, Ni-P coating, alginate microgels, corrosion resistance, EIS test

Introduction

Coatings are used to protect metal products in corrosive environments. These include metallic and non-metallic (polymers or oxides) coatings. Self-healing coatings are of particular interest due to their enhanced durability. The self-healing mechanism is derived from the formation of a protective oxide film at the damage site. For self-healing, anti-corrosion coatings, the active component was, until recently, based on a chromium compound, specifically Cr(VI). However, the introduction of restrictions on the use of compounds containing Cr(VI), resulting from their carcinogenicity, has become the impetus for the development of alternative coatings. In the context of wear resistance, hardness and corrosion resistance, nickel-phosphorous (Ni-P) coatings are comparable to chromium coatings. Although Ni-P coatings do not currently have the ability to regenerate, a viable solution to this problem is the encapsulation of corrosion inhibitors and the introduction of the capsules into the matrix of the coating. This approach has been described for electrochemically-generated nickel [1] and zinc [2] coatings. In these cases, the researchers prepared nanocarriers without any active substances. One example is a Ni-nanocontainer composite coating comprising nanocapsules covered with polyelectrolytes. In the case of a self-healing protective zinc coating [2], nanoaggregates of polyethylene oxide-b-polystyrene (PEO₁₁₃-b-PS₂₁₈) were co-deposited with the zinc compound. The self-healing properties of these systems resulted from the ability of amphiphilic polymers to shrink and swell reversibly.

Alternatively, the self-repair effect of coatings containing capsules loaded with active substances is initiated by appropriate stimuli: temperature changes, radiation, pH changes, pressure changes and mechanical action. In general, the healing mechanism of such coatings depends on the formation of a passive layer and the choice of the active compound depends on the type of substrate requiring protection. A barrier layer for steel is produced by 2-mercaptobenzothiazole, hexamethylene diisocyanate, or linseed oil; whereas for aluminium alloy 2024, Ce³⁺, silyl ester, alkoxy silanes, benzotriazole or 8-hydroxyquinoline [3-7] can be employed. Encapsulating the liquid corrosion inhibitor within the solid matrix can also be achieved by utilising micron-sized gel particles (or microgels). To this end, polyurea microgel particles with 2-methylbenzothiazole (MeBT) have been produced [8].

In this work, a protective Ni-P coating containing alginate microgels charged with nickel salt and sodium hypophosphite, which are the two components essential for electroless metallisation, was prepared. This method provides a novel approach to the formation of self-healing coatings with desirable mechanical properties, including high hardness and wear resistance. A self-repair mechanism is initiated through the reconstruction of the coating at the time damage occurs due to the autocatalytic reaction of nickel deposition. This innovative approach produces a reconditioned surface with identical properties to the original. The use of microgels as a carrier enables a single stage route to the encapsulation of active repair substances, compared with the alternative process of fabricating capsules and subsequently filling them – a process requiring a minimum of two stages. Active substances can in fact be introduced into the microgels during their preparation. The choice of alginate for microgel preparation was indicated by the material's high mechanical strength and the fact that it has limited, negative environmental impact. Furthermore, alginate can use chloride ions as a trigger for self-repair action [9]. This is important especially for protective applications, because solutions containing chloride anions are recognized as one of the most corrosive environments.

Materials and methods

Alginate microgels with diameter of 3-5 μm incorporating nickel chloride and sodium hypophosphite were prepared by the water-in-oil emulsion method.

Ni-P\alginate microgels coatings were prepared by the electroless method as reported elsewhere [10-13]. To 100 cm^3 of a basic bath, - containing a nickel salt, together with reducing, complexing and buffering agents - 0.3 g of alginate microgels loaded with nickel salt and sodium hypophosphite were introduced. The thickness of the coating on the alloy steel substrate (AISI 304) was estimated to be 5 μm by the gravimetric method (EN ISO 1460). The typical fine-grained cauliflower-like surface morphology of the Ni-P coatings was observed using a scanning electron microscope (VEGA II SBH) (Fig. 1).

Electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the performance of the coating in corrosive media [10]. The area of the working electrode exposed to the NaCl solution was 0.352 cm^2 .

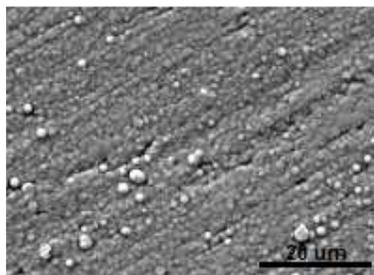


Fig.1 Scanning electron microphotograph of Ni-P coating with alginate based microgels.

Results and discussion

Fig. 2 shows the impedance spectra recorded during 72 hours of immersion in 0.5 mol dm^{-3} NaCl solution. Due to the dynamic nature of the system, three equivalent electrical circuits were employed. In each model, capacitances were replaced with a constant phase element (CPE) due to the deviations from the ideal capacitive behaviour. Model 1 (spectra between 3-7 h of exposure) is composed of the solution resistance (R_1); passive layer capacitance (CPE1); passive layer resistance (R_2); double layer capacitance (CPE2); and charge transfer resistance (R_3) (Fig. 3a). Introduction of the combination of R_4 and L_1 in series was necessary because of the presence of an inductive loop at lower frequencies. In model 2 (spectra between 10-24 h of exposure), Fig. 3b, the resistance (R_3) of charge transfer reaction was replaced by a finite length Warburg element (W_s). In impedance spectra recorded after 36 h of exposure, a third time constant appears. As a consequence, a modification to model 2 was required. In model 3 (spectra between 36-72 h of exposure), Fig. 3c, element R_1 corresponds to the resistance of the NaCl solution; CPE1 and R_2 relate to the capacitive and resistive responses of the relaxation process; CPE2 and R_3 are coating capacitance and resistance; whilst the parallel connection of elements CPE3 and W_s correspond to the charge transfer reaction in an electrolyte/metal interface. For the first 24 h of exposure to the NaCl solution, the coating resistance (R_2) decreased gradually from 9510 to 2420 $\Omega \text{ cm}^2$ due to the electrolyte forming conductive pathways due to the degradation of the protective properties of the initially formed passive layer. The Ni-P\alginate microgels coating shows typical barrier behaviour up to 24 h, after which an increase in both the coating's resistance and capacitance is observed. The increase in the coating resistance is undoubtedly connected to the presence of the third time constant in the impedance spectra (Fig. 2). Between 36 and 72 h, the resistance of this time constant (R_2 in model 3) increases from 63 to 137 $\Omega \text{ cm}^2$. Low resistance values, and the fact that the maximum phase angles appear at higher frequencies, are evidence that some intermediate species is adsorbing the active chemicals on the coating's

surface. A new time constant may be due to the occurrence of a new interfacial process [14]. Having confirmed the presence of the nickel salt and sodium hypophosphite in the microgels (they are typically coloured green), the authors propose that this new interfacial process is an autocatalytic reaction leading to the reduction of nickel cations and the deposition of a metallic nickel-phosphorous coating.

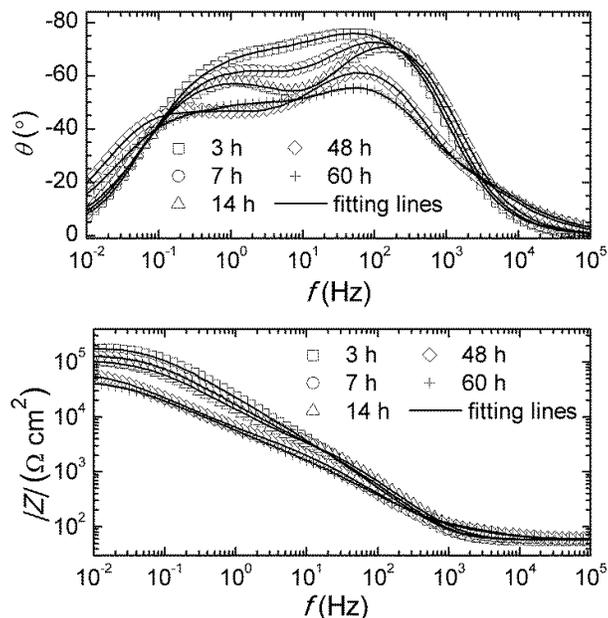


Fig.2 Impedance spectra of Ni-P\alginate microgels coatings recorded after 3-60 h of immersion in 0.5 mol dm^{-3} NaCl solution. Solid lines represent the calculated spectra.

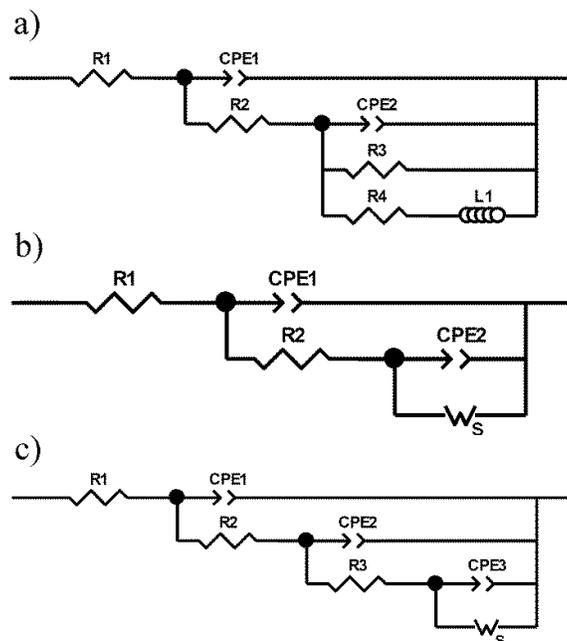


Fig.3 Models of equivalent circuits proposed for curve fitting of EIS data: a) model 1: $R_1(CPE1[R_2(CPE2[R_3[R_4 L_1]])]])$; b) model 2: $R_1(CPE1[R_2(CPE2 W_s)])$; c) model 3: $R_1(CPE1[R_2(CPE2[R_3(CPE3 W_s)])])$.

Conclusions

In summary, a protective Ni-P\alginate microgels coating was prepared by an electroless deposition method. The microgels were loaded with nickel chloride and sodium hypophosphite. During the coating's exposure to the corrosive sodium chloride solution (3.5% NaCl), the microgels suffered some damage, released the active compounds which then reacted together to provide an effective repair for the coating. The reaction is believed to take place as a result of an autocatalytic reaction of the Ni-P. This new interfacial process is responsible for the appearance of the third time constant, which was observed using electrochemical impedance spectroscopy.

The key aspects of this novel process are:

- The development of metallic (Ni-P) coatings with a self-regeneration property. The Ni-P self-healing coatings combine the ability to auto-repair whilst maintaining useful properties such as good wear resistance and high hardness, so important in coatings used for corrosion protection.
- The creation of a reconstructed surface with identical properties to the original. This is made possible by selective nickel deposition at the coating's damage sites.
- The use of microgels as a carrier for an active substance. Currently, a corrosion inhibitor is loaded in micro- or nanocapsules.

The production of a carrier with an active compound in a one step process. At present, the production of a carrier with a corrosion inhibitor is obtained in a process with a minimum of two-stages: 1. Capsule preparation; 2. Corrosion inhibitor encapsulation.

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