Surface functionalization by the introduction of self-healing properties into electroless Ni-P coatings

1 Edinburgh Napier UNIVERSITY

2 MANCHESTER 1824 The University of Manchester

3 PAN Instytut Katalizy i Fizykochemii Powierzchni im. Jerzego Habera Polskiej Akademii Nauk

4 UE Uniwersytet Ekonomiczny we Wrocławiu

Alicja Stankiewicz[1], Zoi Kefallinou[2], Grzegorz Mordarski[3], Zofia Jagoda[4], Ben Spencer[2]

ABSTRACT

Ni-P\alginate microgels coatings, as potential metallic protective coatings with self-healing properties, were deposited by the electroless method. The alginate microgels contained nickel chloride and sodium hypophosphite. It was proven that the reduction of nickel ions released from the microgels is possible on the steel and Ni-P coating surface. The self-healing effect of this system was studied by X-ray fluorescence (XRF), chronoamperometry and scanning vibrating electrode technique (SVET). An improved corrosion protection observed here is attributed to the reduction of nickel ions to metallic nickel on the tested surfaces. Differences in the surface concentration of nickel and phosphorous species in the corrosion tested coatings with and without microgels, as evaluated using X-ray Photoelectron Spectroscopy (XPS), provided substantial evidence for the formation of a Ni-P coating from the compounds included in the microgels.

CONTACT

Alicja Stankiewicz
Edinburgh Napier University
Email: a.stankiewicz@napier.ac.uk
Phone: 00441314552318
Website: www.napier.ac.uk

INTRODUCTION

The provision of robust, durable, low-cost, protective coatings is of benefit to local and global economic growth across many industrial sectors. A beneficial feature of a relatively new category of advanced coating material is the ability to self-heal. The self-healing property significantly enhances the durability and resilience of the coated structure. Self-healing coatings are 'active' coatings which have the material capacity to reform over a first scratch or blemish and hence continue to offer corrosion protection to the underlying structure. Self-healing protective coatings investigated so far are mainly based on carrier systems that store self-healing substances [1,2], and most often capsules or fibres are included in the polymeric matrices [3,4].

A new nickel-phosphorous self-healing coating process, which promises enhanced material properties and a low toxicity production process compared to the chromium-based equivalent is proposed. The introduction of microgels comprised of nickel salts and sodium hypophosphite into Ni-P matrices results in the surface functionalisation by the introduction of self-healing properties due to the autocatalytic reaction of nickel and phosphorous deposition:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni + 2H_2PO_3^- + 2H^+ + H_2$$

$$H_2PO_2^- + H \rightarrow P + H_2O + OH^-$$

METHODS AND MATERIALS

Alginate microgels for co-deposition with nickel-based coating were produced by a reverse emulsion method.

Electroplating of nickel coatings on steel samples from Watt's bath was carried out for proof of concept trials.

Electroless deposition of coatings was carried out on steel samples from a bath containing nickel chloride, sodium hypophosphite, sodium citrate, at pH 9 and temperature of 60°C. Coatings of thickness 10.0 ± 0.7 µm were produced.

XRF, chronoamperometry and SVET were used to study the self-healing effect. The morphology of the Ni-P and Ni-P\alginate microgels coatings was examined by SEM. The elemental and chemical composition of the coatings was performed by XPS.

Figure 1. Steel samples covered with electroplated nickel coating after 24 hours in 3.5 wt.% NaCl.

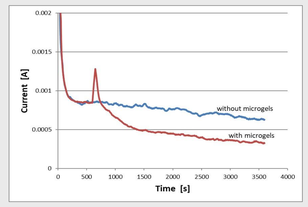

Figure 2. Chronoamperometry of the steel samples immersed in the 3.5 wt.% NaCl solution.

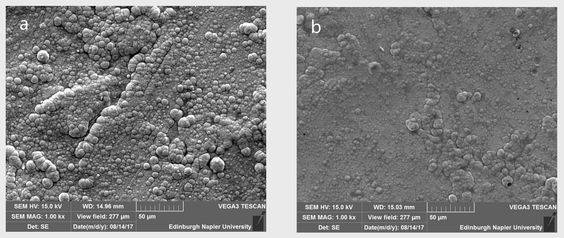

Figure 3. SEM microphotographs of a) Ni-P coating and b) Ni-P\alginate microgels coating.

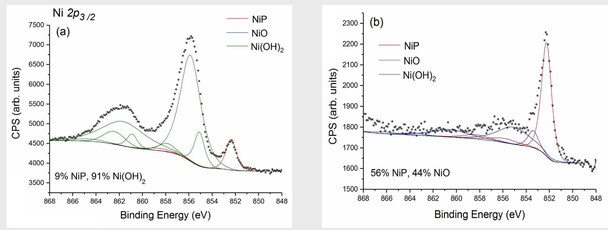

Figure 4. Comparison between the Ni 2p3/2 spectrum for Ni-P and Ni-P\alginate microgels coatings after 6 h of immersion in 3.5 wt.% NaCl solution.

time of immersion, h	Fe	Mn	Co	Ni	Cu	Zn	Cr
0	99.5954	0.1543	0.0241	0	0.1718	0.0444	0
1	97.5356	0.2818	0.4194	1.6996	0.0221	0.0307	0
3	97.3933	0.3072	0.4119	1.8578	0.0165	0	0.0033
24	96.8923	0.2954	0.4068	2.3307	0.0307	0.028	0.0062

Table 1. X-ray fluorescence analysis of the steel sample immersed in 3.5 wt.% NaCl solution containing alginate microgels.

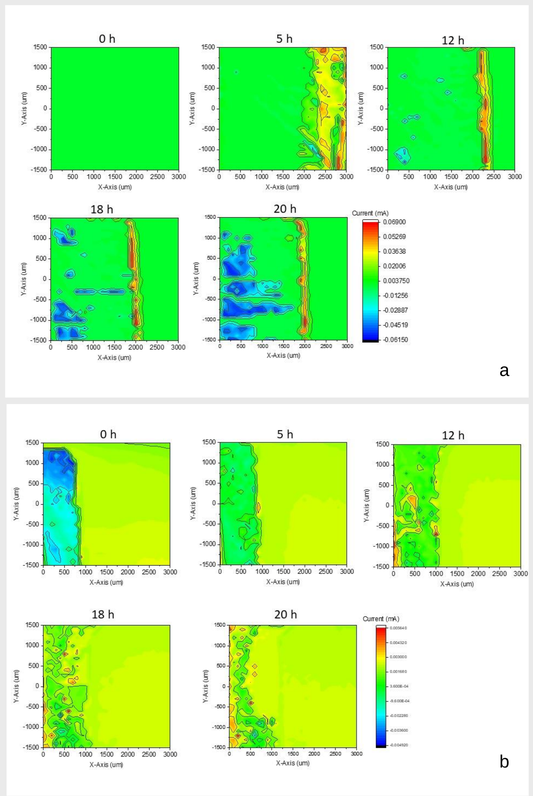

Figure 5. Current density changes above a) Ni-P coating surface and b) Ni-P\alginate microgels coating surface after 0, 5, 12, 18 and 20 h immersion in 50mM NaCl detected by SVET.

RESULTS AND DISCUSSION

Steel specimens covered with thin layer of electroplated nickel coating were immersed in 50 ml of 3.5 wt.% NaCl solution with and without microgels. The sample immersed in NaCl solution without microgels (bottom sample) suffered severe corrosion, Figure 1.

XRF was used to analyse the nickel content on the steel substrates. The nickel content on the steel surface grew from 0 and increased to 2.3% after 24h, Table 1.

The chronoamperometric results showed a decrease in the current flow of the steel surface exposed to the NaCl solution containing microgels compared to the solution without microgels, as shown in Figure 2.

The surface morphology was typical for Ni-P deposits and exhibited a cauliflower-like appearance, whilst the Ni-P\alginate microgels coatings had a smoother surface, Figure 3.

The increase of the concentration of the oxidised nickel species in the Ni-P coating due to anodic dissolution was observed, Figure 4. There was almost no change in amount in NiP in the Ni-P\alginate microgels coating.

The cathodic response was detected on the Ni-P\alginate microgels coating on the beginning of immersion, Figure 5. This behaviour could indicate a self-healing activity based on the nickel reduction.

CONCLUSIONS

The alginate microgels are promising candidates as carriers of nickel chloride and sodium hypophosphite for the Ni-P coating functionalisation.

The SVET analysis confirmed that the Ni-P\alginate microgels coating therefore has self-healing properties.

It is important to highlight that the reconstruction effect based on the autocatalytic deposition of nickel provides a self-repaired surface with similar properties to the original.

REFERENCES

1. A.P. Esser-Kahn et al., Macromolecules. 44 (2011) 5539–5553.
2. S.H. Cho et al., Adv. Mater. 21 (2009) 645–649.
3. V. Karpakam et al., Electrochim. Acta. 56 (2011) 2165–2173.
4. A. Latnikova et al., Soft Matter. 8 (2012) 10837.