



Embedded magnetic nanoparticle sensors for monitoring primer failure beneath paint



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ABSTRACT

Magnetic nanoparticles embedded into anti-corrosion primer coatings are demonstrated as potential sensors for the depletion of corrosion inhibitor molecules. In corrosive environments these nanoparticles are chemically transformed to species that have different structural and magnetic properties. By monitoring changes in their magnetic state in such environments, strong correlations between the particles' magnetic state and the amount of remaining inhibitor molecules can be established, enabling a novel sensing approach that is both non-destructive and non-contact. Herein we demonstrate the transformation of the magnetic particles via characterisation of their magnetic and material properties after aqueous ageing at different pH, by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and vibrating sample magnetometry (VSM). Furthermore, a non-destructive approach for monitoring the magnetic particles that have been placed in coatings, through their interactions with alternating magnetic fields, is also proposed.

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1. Introduction

Early warning of materials and structure degradation can lead to significant savings in maintenance practices, particularly for the aerospace industry [1]. Monitoring corrosion of metals remains a challenge and increasingly many novel approaches are being investigated to provide early indication of corrosion state [2–5].

The use of chromate inhibited primers is critical for the protection of high strength aluminium alloy and other light weight alloy components. The performance of these primers enables aircraft to operate with minimal corrosion issues for up to 50 years without disassembly [6–8]. This is quite remarkable considering that high strength aluminium alloys are highly susceptible to corrosion due to their heavy loading with copper, which leads to the presence of strong localised galvanic corrosion cells. The success of inhibited primers has little to do with organic barrier properties, rather is predominantly due to good adhesion to the metal substrate and to the high levels of chromate pigments.

To avoid corrosion-related catastrophic failure it is of paramount importance that the amount of corrosion inhibitor remaining within primer does not deplete to the extent that passivation

against corrosion is jeopardised. Therefore, we propose the use of sensory nanoparticles that can be embedded into the inhibitor loaded primers that can be externally and non-invasively probed to monitor changes in chromate (or possibly other) inhibitor concentrations, and would thus enable the status of the primer to be determined even prior to the onset of corrosion. Due to the uncertainty in failure mechanisms there is a need for monitoring at high spatial resolution such that microscopic flaws in paint films and localised corrosion processes can be understood and related to the performance of larger structures. It follows that this information is important for guiding the development of new materials with improved performance and reliability.

Magnetic iron oxide nanoparticles are used in a number of fields including data storage and magnetic resonance imaging as both contrast agents and for cell targeting/labelling [9–13]. In such applications, the local environment of the magnetic iron oxide nanoparticles can greatly affect their stability and their properties. Changing their ambient conditions may result in transformations to other iron based phases, which can not only affect the particles' magnetisation, but may also cause them to cease performing their intended functions.

Based on the notion above, we set about exploring the use of magnetic nanoparticles that may serve as indicators for corrosive conditions. The concept centres on embedding magnetic nanoparticles into coatings and monitoring their chemical transformation under corrosive conditions from species that are strongly magnetic

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to those which possess little or no magnetism, with the degree of magnetism being indicative of the level of corrosion. The three iron oxides: Fe_3O_4 (magnetite), $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) are ferrimagnetic and yield a ferromagnetic response at room temperature. The three principle hydrated species are the oxyhydroxides $\alpha\text{-FeOOH}$ (goethite), $\gamma\text{-FeOOH}$ (lepidocrocite), and $\beta\text{-FeOOH}$ (akaganéite), which are antiferromagnetic and yield a weak paramagnetic-like response at room temperature. Other hydrated iron oxide species such as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are also antiferromagnetic [14], and when formed (e.g. via corrosive action), will not contribute significantly to a bulk magnetic response.

In this study, maghemite nanoparticles have been embedded into an aerospace primer matrix which was then used to coat panels of aluminium AA2024 alloy. The coated panels were then subjected to a series of accelerated corrosion test and subsequently analysed by Raman spectroscopy. Additionally, in separate tests, maghemite nanoparticles were aged in aqueous solutions of different pH for various time periods and then characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM) and with a vibrating sample magnetometer (VSM). This was carried out to determine and explore the various transformations that may occur, and the particles' solubility. The degree of the magnetic behaviour of the iron oxides ultimately depends on the crystal structure, particle size, the extent of cation substitution [15] and hence these aspects were also monitored. We also propose an approach for non-destructive sensing of the magnetic nanoparticles in coatings, which involves measuring their response to applied alternating magnetic fields.

2. Experimental

2.1. Procedures

Maghemite nanopowders were purchased from Sigma Aldrich (Product No. 637106) and utilised throughout this study. For the aqueous ageing studies, five grams of the powder was placed into sample vials, to which 15 mL aqueous solutions (18.2 M Ω MilliQ water) of either pH 2, 7, 11 was added. The sample vials were placed in a water bath heated to 50 °C, and the pH of each solution was readjusted fortnightly using HCl and NaOH. At the end of ageing the specimens were dried in a vacuum oven operated at ambient temperatures, typically taking 48 h to completely dry.

For the accelerated corrosion tests, the magnetic nanoparticles were dispersed into a commercial aerospace primer resin (Sterling Lacquer Mfg. Co, USA). AA2024 panels of size 30 mm \times 30 mm \times 1.6 mm (Kaiser Aluminium) were ground and polished down to a 1 μm finish with diamond paste and subsequently coated with the maghemite loaded aerospace primer. Accelerated corrosion testing was carried out in accordance with the modified GM9540P test using 1% NaCl acidified to pH 4 using H_2SO_4 , in which the panels were positioned at 30° to vertical and faced three spray nozzles located at the rear of the chamber (Model CC1000, Ascott Analytical Equipment Ltd.)

Powder XRD measurements were carried out with a Bruker D8 diffractometer using a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) within a 2θ range of 10°–85°. The mean crystallite size (d_{av}) for the sample was determined from a Rietveld refinement incorporating the Scherrer formula.

TEM images were taken on a Philips CM-30 microscope with a 200 kV accelerating voltage. SEM images were obtained on an FEI nanosystems 400 nanosem equipped with a FEG source.

Raman spectroscopy was performed on a Renishaw inVia confocal microscope system. Specimens were illuminated with an argon laser (514 nm wavelength) through a 50 \times objective. The incident laser power set at 0.5 mW, and the spot was estimated to be in the range of 1 μm . Spectra were collected over the wavenumber

range of 200–1800 cm^{-1} over the surface of the coatings, and each spectrum was averaged over 10 scans.

Magnetisation measurements were performed using a Lake Shore 7300 Series vibrating sample magnetometer (VSM) with a 2 T electromagnet. The maghemite nanoparticles were dispersed into a glue matrix according to the following procedure: iron oxide nanoparticles (20–60 mg) were weighed into size 4 pharmaceutical capsules and a small amount of 5-min Araldite™ was added to wet the particles. The nanoparticle-glue mixture was homogenised with a small wooden stirrer that was then cut to fit within the capsule, which was subsequently sealed.

2.2. Characterisation of starting material

Fig. 1 shows the XRD pattern and room temperature magnetisation curve (magnetisation versus applied magnetic field) of the as-received maghemite nanopowder, labelled by the manufacturer as iron (II, III) oxide, with mean particle size <50 nm, surface area 60 m^2/g . The untreated nanoparticles possess a saturation magnetisation, M_s , of around 70 $\text{A m}^2/\text{kg}$ and coercivity ($\mu_0 H$) of around 78 mT. The value of M_s falls within the range typically expected for maghemite (60–80), whereas for magnetite the value is typically above 90 $\text{A m}^2/\text{kg}$ [14,16]. The remnant magnetisation, M_r , is around 11 $\text{A m}^2/\text{kg}$.

Since both magnetite and maghemite have a spinel structure, their XRD patterns are very similar, mainly differing by the presence (or absence) of a few weak reflections. The lattice constant, a , was found to be 8.33 \AA , and the relative peak intensities confirm the specimen is maghemite. The absence of reflections at 14.9°, 20.7°, and 26.2° imply the starting material is not the tetragonal, vacancy ordered form, but rather the cubic, disordered form of maghemite [17,18]. The average crystallite size, as determined from a Rietveld refinement was found to be 40 nm. Hematite, which possesses the trigonal corundum structure, has a clearly different XRD pattern. The reflections at around 33.2°, 40.8°, and 64.1° (indicated by * in the figure) can be attributed to hematite, whereas those at 24° and 49.5° may correspond to maghemite (2 1 0) and (4 2 1) respectively, or to hematite (0 1 2) and (0 2 4) respectively. Further evidence that

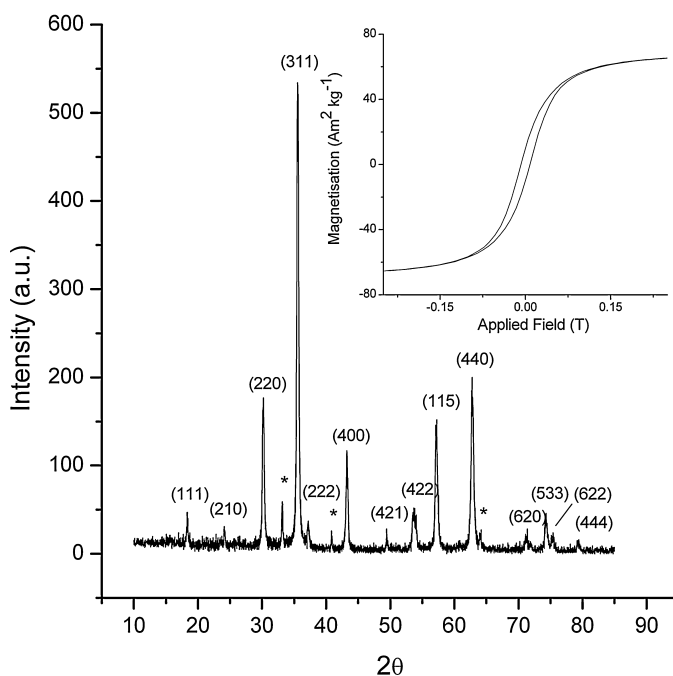


Fig. 1. XRD pattern of the as-received Fe oxide nanopowder (magnetisation curve shown in the inset).

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