Original manuscript
of the Proceedings:

Scharnagl, N.; Korrapati, V.; Maia, F.; Mata, D.; Spacek, V.; Galvao, T.; Tedim, J.:

Corrosion Sensing for Mg alloys by Nanocontainer including Coatings

Corrosion Sensing for Mg alloys by Nanocontainer including Coatings

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Abstract

For the application of Mg alloys corrosion is mostly a challenge. Therefore, the early detection of corrosion for Mg based materials is important for automobile and aeronautic industry. The work introduces sensing coatings for metallic corrosion detection at an early stage that will help to mitigate the costs of corrosion through continuous monitoring. Following a scientific step by step approach: (i) selection of appropriate pH indicators for detection of corrosion, (ii) loading of indicating molecules into nanostructured materials with controlled release capabilities, and (iii) incorporation of the resulting materials into coating formulations with varied chemistries lead to a potential indicator system. Phenolphthalein encapsulated silica nano-capsules, which were incorporated into solvent based polymeric formulations, result in novel corrosion sensing coatings for Mg alloys with improved functionality and standard performance. The resulting modified formulations were tested on AZ31 as well as on an experimental Al-free Mg alloy, and compared against formulations with pH indicators directly dispersed on the surface. Additionally, the functionalized coatings were characterized by several spectroscopic methods (IR, Raman) as well as by SEM / EDX. Furthermore, the ability of the coatings to detect corrosion by color change was validated by immersion and salt-spray tests.

Keywords: Mg alloy, functionalized coating, pH sensors

1. Introduction

Magnesium is well known as an advanced engineering material with remarkable properties, proven in countless applications. Beyond its widely reported properties, such as high strength-to-weight ratio, the top listed shortcoming of magnesium and its alloys has always been their low corrosion resistance [1, 2]. This has hindered its

applications, particularly in structural ones, across a broad range of industrial sectors from automotive to medical.

For suitable corrosion protection systems for magnesium alloys, some successful results have already been used in technical applications.[3-5] Various approaches were used to combat galvanic corrosion in impure magnesium or common magnesium alloys, for example, by alloying with rare-earth elements [6] to reduce the potential of galvanic coupling, or simply by chemically etching of the material to reduce the presence of non-alloying elements like Fe, Cu or Ni and other contaminants [7, 8]. A number of efforts have been made to find suitable coatings including plating, conversion coatings and organic coatings. These act as electrical, physical or physico-chemical barriers between magnesium or other metals (galvanic coupling) and the corrosive environment. Among commonly used polymer based coatings are polyacrylates, polyurethanes, polyesters, polypyrroles, and epoxies. Promising polyetherimide (PEI) with self-healing properties was found in the investigation of other polymer classes for the corrosion protection of magnesium.[9, 10] Overall, they represent technical requisites to enhance corrosion protection, as well as an important outstanding adhesion [10]. However, most polymer-based systems cannot prevent the partial penetration of corrosive. Ultimately, this leads to corrosion of magnesium and destruction of the native $Mg(OH)_2$ protective layer, finally loss of the coating and, as a result, the loss of corrosion protection.

An improvement for polymeric coatings is a complementary corrosion signaling system, which is able to spot corrosion events and make them detectable by visual inspection. Timely detection of corrosion prevents its propagation and allows rapid repair of the damaged component, which in turn reduces maintenance costs.

Phenolphthalein (PhPh) based pH-sensing systems as pH-Indicator have been proven to be highly efficient to early detect corrosion events [11, 12], including silicon nano-capsules containing PhPh (SiNCs-PhPh) ones. Upon onset of corrosion, the hydroxide anions (OH^-) formed on the cathodic site change the color of the PhPh to strong pink within the range of pH 8.2 - 12, which will then easily spot these sites for visual inspection.[12] This work focuses on studies of optimization and validation of the pH-sensing functionality of SiNCs-PhPh containing polymeric coatings on Mg alloy substrates.

2. Results and Discussion

2.1 Materials and Methods

Metal substrates of AZ31 magnesium alloy with the following composition (wt. %) were used: Al 2.970%, Zn 0.845%, Mn 0.236%, Si 0.0226%, Cu 0.002%, Ca 0.003%, Ni 0.004%, Fe 0.026%, balance Mg.

All chemicals used are of analytical grade: dichloromethane (DCM, ≥99.8%, Merck), N,N'-dimethylacetamide (DMAc, ≥99.8%, Merck), poly(ether imide) (PEI, Ultem® 1000, General Electric), polyurethane (PUR, LACQUER AQ CC 080 Synpo, CZ),

epoxy (CHS-EPOXY 573, Synpo, CZ). phenolphthalein (PhPh) loaded silicon oxide nano-sized capsules (SiNCs-PhPh, ADDPRIME®, Smallmatek).

Scanning electron microscopy (SEM, Tescan Vega3 SB) operated at an acceleration voltage of 8 kV with a working distance of 6 mm was used to examine the morphology of the prepared coatings. The equipment is coupled with an energy dispersive X-ray (EDX) spectrometer detector used performing distribution analyses of the Si Kα-shell signal of the SiNC-PhPh.

Confocal Raman spectroscopy (Bruker, Senterra) was applied to perform 3D mapping analysis of the final coatings to evaluate the distribution of the SiNC-PhPh particles in the volume of polymer matrix. All spectra were collected with an excitation wavelength of 532 nm, laser power of 5 mW, aperture of 25 µm and 256 scans for an appropriate signal-to-noise ration with an integration time of 2s.

Electrochemical impedance spectroscopy (EIS) was performed at room temperature (21°C) using a three-electrode cell assembly with a platinum electrode as the counter electrode, coated Mg alloy sample as the working electrode (exposed area of 0.5 cm^2) and a Ag/AgCl electrode as the reference. An aqueous solution of 0.5 M NaCl (350 ml) was used as the electrolyte. To avoid the interference from external electromagnetic fields all tests were performed inside a Faraday cage. The measurements were done using a Gamry Reference 600 potentiostat at different immersion times up to 3 weeks.

2.2 Discussion of Results

Fig. 1 shows a set of SEM and EDX mapping images of freestanding polymer films including 5 wt-% SiNC-PhPh related to polymer concentration prepared by three different protocols.

a) SiNC-PhPh directly added to the polymer (PEI) solution (800 rpm for 1h)

b) SiNC-PhPh predispersed in solvent (650 rpm 1h) and then added to polymer (PEI) solution (800rpm for 1h)

c) SiNC-PhPh predispersed in solvent (500 rpm 5h) and then added to polymer (PEI) solution (800rpm for 1h)

The mapping of the Si signal gives an indication of the distribution of the SiNC-PhPh (Figs 1b, e and h). Taking into account the average particle size values presented in the histogram plots (Figs. 1c, f and j), almost all particles have the same size. Nevertheless, it becomes evident that protocol 3 leads to the best particle size distribution among the other two, being the only one that fits to the shape of a Gauss curve (inset plot of Fig. 1j). Additionally, the superior performance of protocol 3 is supported by the presence of particle agglomerates below 1 µm.

In dense coatings, differences on the impedance curves are observed (Figs. 2a and b). It seems that at the beginning the content of SiNC-PhPh slightly increase the impedance values of the coatings about one order of magnitude. This indicates that the nanoparticles reduce swelling behavior and the diffusion of electrolyte. The bare coatings without SiNC-PhPh (Fig. 2a) show three time constants, a resistive behavior (R_{Coat}) and weak corrosion activity events (R_{ct} and C_{dl}). The coatings with SiNC-PhPh

show an almost impeccable capacitive behavior for the first hour of immersion (Fig. 2b). Nevertheless, impedance reaches the value of the particle free coating after about 6 hours, indicating a started swelling process and therefore corrosion activities.
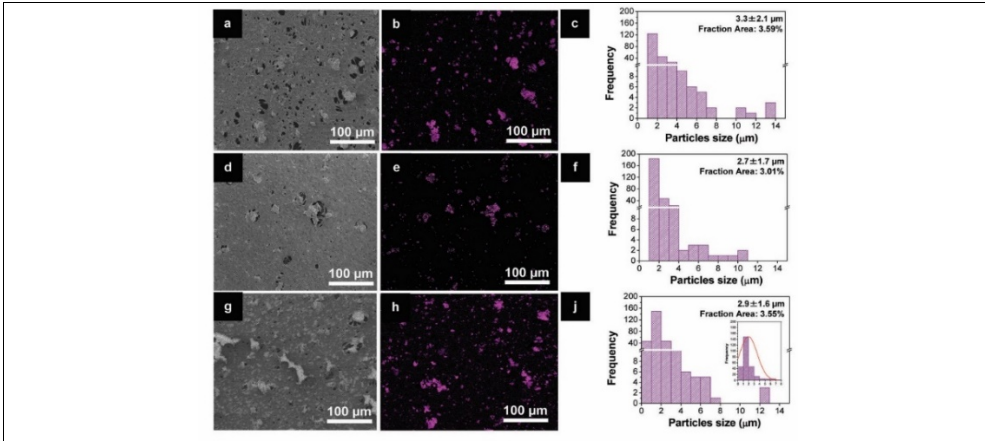

Figure 1: SEM images, EDX mappings and particle distribution of SiNC-PhPh in polymer formulations by different protocols.
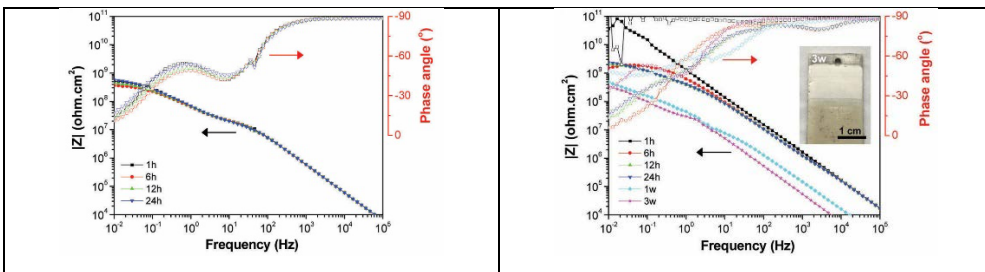

Figure 2: Bode and phase angle plots of the AZ31 panels coated with coatings of (a) pure PEI and (b) 5 wt.% SiNC-PhPh/PEI after up to 3 weeks of immersion in 0.5 M NaCl solution. Inset: photograph image of the sample after 3 weeks

In principle, this demonstrates that the incorporation of particles is not decreasing the barrier properties of a polymeric coating. However, RAMAN investigations validated that the particles are more or less homogenous distributed all over the bulk of the polymer matrix.
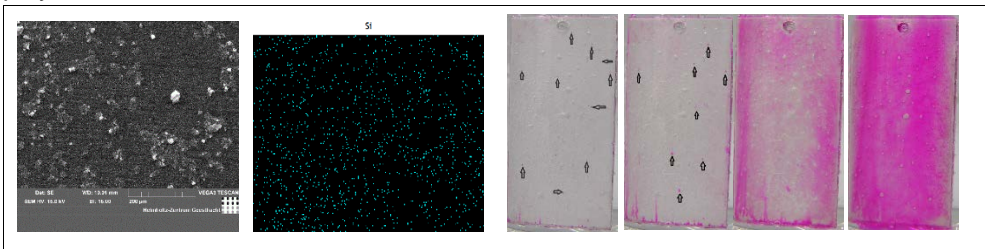

Figure 3: From left to right: SiNC-PhPh particles distributed on cleaned AZ31 by isopropanol - SEM morphology, EDX of Si and control of pH-sensitivity immersing in 0.5 wt% NaCl @ RT (series of 5, 15, 60 and 300 sec). Arrow marks pointing some agglomerates seen after 5 and 15 seconds.

Therefore, the signalling effect by colour change could not be assigned to the pH change of the Mg alloy surface directly but by an alkaline environment all over the

coating matrix. Direct impregnation of the metal with SiNC-PhPh particles before any polymeric coating should offer the possibility to overcome this gap. 5 wt-% of SiNC-PhPh were emulsified in acetone, propanol-2 or dichloromethane and metal substrates treated by dip-coating with the solutions. Figure 3 demonstrates the improvement of particle distribution on the surface of the metal and the signalling effect caused by the change of the Mg surface towards alkaline values.
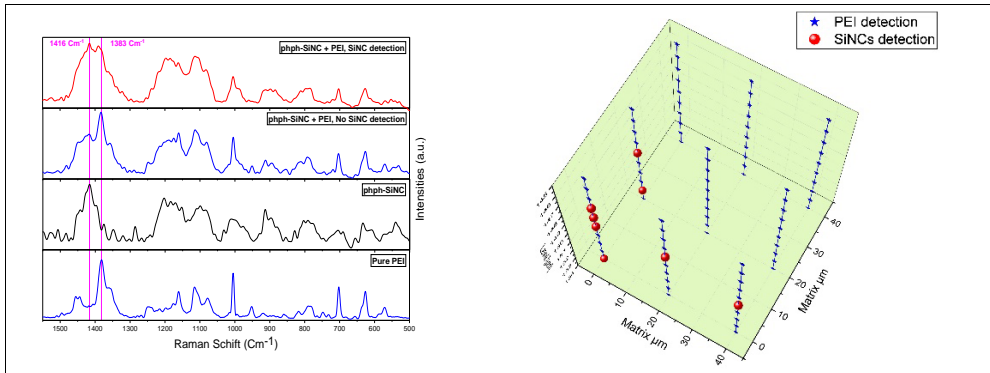

Figure 4: Raman characterization of the pure PEI polymer matrix and with SiNC-PhPh (left) as well as their distribution over set of 9-data points in a depth-profiled matrix (10 layers each 1µm distance) (right). Blue dots represent pure polymer and red dots represent SiNC-PhPh detection.

After the pre-treatment with the SiNC-PhPh emulsions, coatings with particle free polymer formulations were carried out and the resulting specimen investigated by 3D Raman mappings. Figure 4 shows the result of the characterization. Raman shift of 1416 cm^{-1} and 1383 cm^{-1} were assigned to the SiNC particles respectively to the polymer. Unfortunately, still the particles are not oriented to the surface but also to the matrix. Obviously, the coating solution dissolved the particles from the surface and lead to a distribution in the polymer bulk.
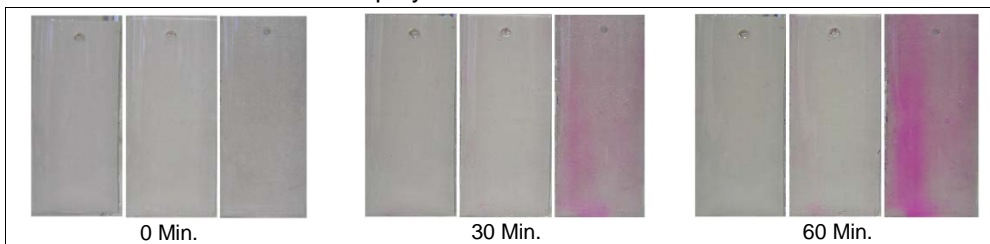

Figure 5: Series of 1, 3, 5-wt% SiNC-PhPh distributed by CH$_2$Cl$_2$ coated by 5-wt% of polymer (PEI) in CH$_2$Cl$_2$ during salt immersion tests in 0.5 wt% NaCl solution @RT (0Min, 30Min, 60Min)

Unlike from propanol-2, SiNC-PhPh distributed in dichloromethane show a very homogeneous layer without clusters and the polymer coatings appear to be defect free. Border-effects and granule-effects are highly minimized by using CH$_2$Cl$_2$ as solvent for the pre-conditioning. Specimen with these combined coatings and particle concentrations of 1, 3 and 5 wt-% were extended to salt immersion tests in 0.5 wt% NaCl @ RT solution. Photographs were captured at 0min, 30min and 60min. However, all concentrations of SiNC-PhPh exhibit stable resistance under chlorine attack up to 24 hours. Then depletion of polymer starts in the form of surface pickling.

Nevertheless, the signalling behaviour of the particles shows a homogeneous pH-change to an alkaline pH of the metal. Concentrations starting with 3 wt-% of SiNC-PhPh show a significant colour change and demonstrate a well performing signalling effect. Diffusion of Cl^- and OH^- ions from solution onto the metal surface, passing the protective polymer layer, is relatively fast and can dramatically accelerate the corrosion by dissolution of magnesium on long exposures.

3. Conclusions

Polymeric coatings loaded with SiNC-PhPh particles work as efficient pH-sensing and signaling systems, by spotting early corrosion events on Mg alloys due to local change of color. This allows identification by visual inspection. A 3 wt-% concentration related to the polymer fraction offers pH-sensing signaling functionality. SiNC-PhPh particles tend to agglomerate in polymeric solutions, while by direct coating the distribution is more homogenous and can be sealed or protected by final polymeric layers. For the future other sensor systems with signaling functionality seems to be possible, e.g. for UV or mechanical influences from the environment.

Acknowledgements

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