

Zinc phosphate micro flakes as new corrosion inhibition additives

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ABSTRACT

The use of zinc phosphate micro flakes as fillers in corrosion protective coatings was investigated. In this paper, we present the synthesis of zinc phosphate particles having a specific morphology exhibiting a large surface to volume ratio and thus enhancing the reactivity of zinc phosphate towards corrosive medias.

The in-house synthesized zinc phosphate micro flakes show an improved corrosion protection on mild steel. Their performance was first tested as dispersions in a standard corrosion testing electrolyte. Furthermore their overall resistance towards corrosion was demonstrated as they were used as fillers in an epoxy-based coating spin coated on mild steel. When compared to commercial zinc phosphate particles incorporated in the same matrix, the micro flakes present overall resistance values of about one decade higher.

Keywords: zinc phosphate, corrosion protection, mild steel, polymer coating, nanocomposite

1 INTRODUCTION

Corrosion protection is a constant concern to steel manufacturers and users. Zinc phosphates were often used as protective films directly grown on a metal surface by conversion reaction or as particulate additives in a coating^[1, 2, 3]. The use of spherical zinc phosphate pigments limits their protective action because of their limited surface to volume ratio and their intrinsic low solubility. Such combination hinders the active components to be liberated fast enough to prevent corrosion. Modifying the particles morphology by increasing their aspect ratio / surface to volume ratio is one strategy to improve the particle efficiency against corrosion.

2 EXPERIMENTAL PART

2.1 Zinc phosphate micro flakes synthesis

All the precursors were ordered from Sigma Aldrich. The zinc phosphate micro flakes were synthesized by a precipitation technique as described elsewhere^[4]. The micro flakes morphology was obtained by adjusting the amount of citric acid in the reaction vessel. When the precipitation of zinc phosphate started, the solution was kept under constant temperature and stirring for 48 h. The precipitate was then

collected by centrifugation and rinsed with D.I. water 3 times and was finally dried for 12 h at 40 °C under vacuum.

2.2 Polymeric matrix synthesis and coating

The commercial zinc phosphate particles and the synthesized micro-flakes were dispersed in a UV curable epoxy matrix containing a reactive diluent. The obtained paints were spin coated on mild steel substrates (ST1203) previously cleaned with an alkaline bath Surtec 138 and subsequently UV cured with a UV Hg-lamp (Baltron).

2.3 Characterization

The structure of the synthesized particles was accessed by X-Ray diffraction analysis using a powder diffractometer D8-Advanced (Broker-AXS). The particles morphology and distribution in the polymeric matrix were observed using scanning electron microscopy SEM (Quanta 400 F - FEI).

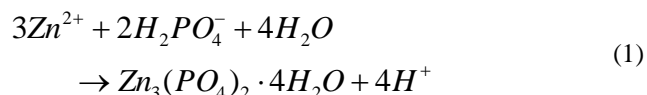
The corrosion protection properties of the particles were demonstrated by immersing mild steel substrates ST1203 in 3.5 wt.% NaCl electrolytes containing either no zinc phosphate powder, or commercial zinc phosphate powder or in-house synthesized zinc phosphate micro flakes.

Further electrochemical characterization was performed using a SP-240 potentiostat-galvanostat equipped with an impedance spectroscopy board (Bio-Logic). A Pt coiled wire (23 cm²) was used as a counter electrode and a Ag/AgCl in 3M NaCl as reference electrode.

3 RESULTS AND DISCUSSION

3.1 Synthesis of the zinc phosphate micro flakes

The precipitation of the zinc phosphate particles occurs according to the following reaction:



The micro flake structure of the zinc phosphate was controlled by adding in the reaction vessel an acid having at least 2 acids groups such as citric acid. The following figures show SEM images of zinc phosphate particles

obtained without (Figure 1) and with (Figure 2) the addition of citric acid in the synthesis solution.

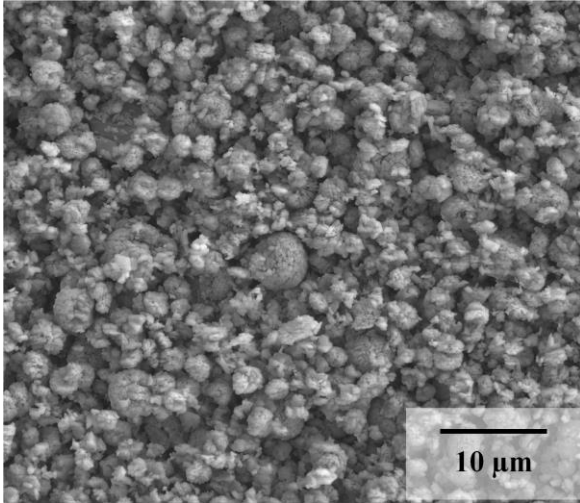


Figure 1: SEM image of zinc phosphate particles synthesized without citric acid.

The micro-flake shape of the zinc phosphate particles is expected to lead to improved corrosion protection properties when compared to standard micro-sized zinc phosphate particles as they have a higher surface to volume ratio. Furthermore, the flake-type shape is preferred to nanosized particles when dispersed in a matrix as the flakes can be oriented parallel to the metal substrate surface and in this way, can improve the coating barrier properties. The permeation path to the substrate is longer because of the increased tortuosity .

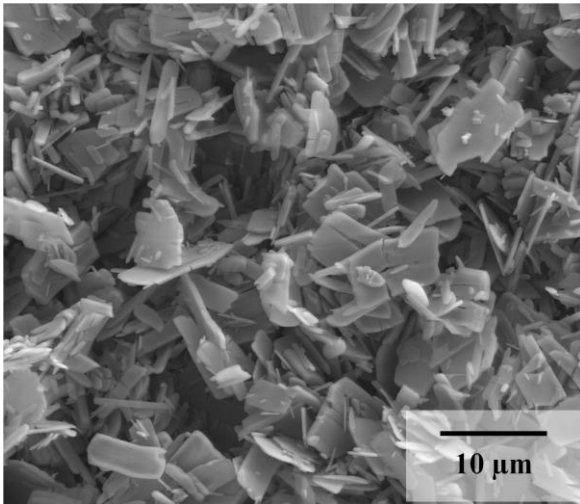


Figure 2: SEM image of zinc phosphate particles synthesized with citric acid.

The synthesis of the zinc phosphate micro-flakes was upscaled from a 20 ml reaction vessel to a 4 liter reactor which allows for a more precise control of the bath temperature and of the stirring conditions. This small

upscaling was performed in order to identify the key parameters to be controlled for a larger scale synthesis of the zinc phosphate micro-flakes. The precipitates obtained in the 4 l reactor were further characterized and compared to the powders obtained at the lab-scale. X-ray diffraction analysis confirmed that zinc phosphate (as Hopeite _ pdf 01-076-0896) was synthesized as shown in Figure 3. Scanning electron microscopy was used to prove that the particular micro-flakes morphology of the zinc phosphate particles was maintained (not shown here).

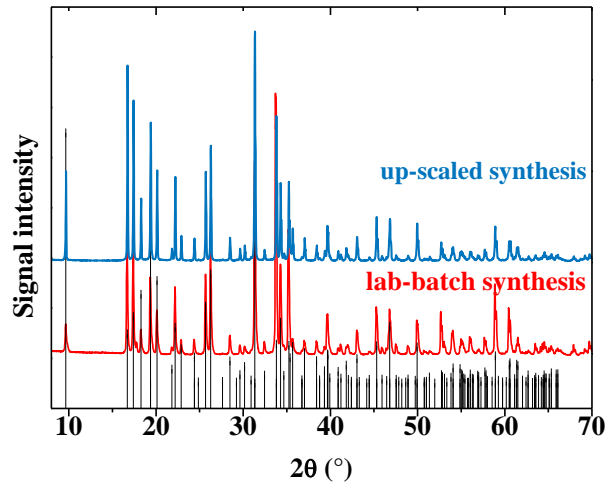


Figure 3: X-Ray diffraction spectrum of zinc phosphate micro-flakes synthesized at the lab scale and at a larger scale. The black lines correspond to the pdf 01-076-0896 reference file.

The micro flakes morphology appeared not only to be dependent on the addition of citric acid but it also required to limit the precipitation reaction speed by maintaining the bath temperature to values lower than 30 °C and stirring at speeds not higher than 300 rpm.

3.2 Mild steel corrosion in solutions containing zinc phosphate micro-flakes

To investigate the ability of zinc phosphate to protect mild steel from corrosion, the particles were first tested as such after dispersion in a standard test electrolyte. Mild steel substrates preliminary degreased with acetone were immersed in 3 different test solutions: a standard solution of 3.5 wt% NaCl in H₂O and 2 solutions of 3.5 wt% NaCl in H₂O containing dispersed zinc phosphate microparticles. For one solution the particles were commercially available zinc phosphate microparticle whereas the other solution contained the synthesized zinc phosphate micro flakes. The overall resistance of the steel plates was measured in the different solutions after 10 minutes and 1, 2 and 3 days of immersion by means of electrochemical impedance spectroscopy. The obtained impedance data are shown in the Figure 4.

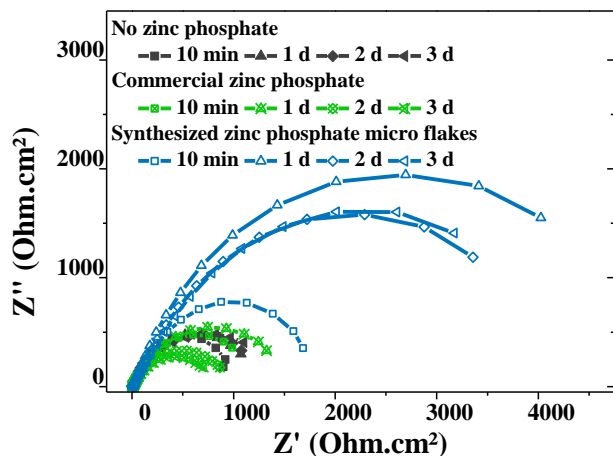


Figure 4: Nyquist representation of the impedance of mild steel immersed in solutions containing: no zinc phosphate, commercial zinc phosphate microparticles, synthesized zinc phosphate micro flakes particles.

After 10 minutes of immersion in the different electrolytes, a larger impedance was already measured for the steel plate immersed in the solution containing the zinc phosphate micro flakes. This indicated that a protective thin layer built up on the steel surface. This layer seemed to stabilized after 2 days of immersion.

Visual observation of the steel substrate over the 3 days of immersion revealed that as expected corrosion points were fast appearing on the steel substrate immersed in the reference solution and did quickly spread. The sample immersed in the solution containing the commercial particles did also show signs of corrosion rapidly although one could observe, on a few points, the formation of white deposits associated to the formation of some passivation products: iron phosphate or zinc oxide.

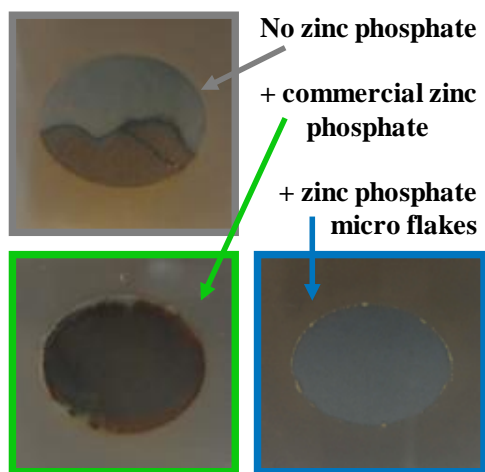


Figure 5: pictures of mild steel substrates after 1 day of immersion in the reference solution (top left), in a solution containing commercial zinc phosphate particles (down left) and in a solution containing zinc phosphate micro flakes.

On the other hand, corrosion points on the steel immersed in the solution containing the micro flakes did not appear before 3 days of immersion. A white deposit was visible on the edges of the steel disc and was associated to the formation of passivation products. Pictures of the steel surface after 1 day of immersion in the different solutions are grouped in Figure 5.

In order to highlight the passivating character of the zinc phosphate micro flakes when dispersed in solution, the steel substrates were also polarized from open circuit potential (OCP) to + 250 mV vs OCP at a scan rate of 10 mV/s. The current measured for each steel substrate after 10 min and 3 days of immersion is plotted in Figure 6.

After 10 minutes of immersion in the 3 different electrolytes, the steel plates had already different open circuit potentials indicating a different surface state. When increasing the potential, a first increase of current is observed for the plate immersed in the standard electrolyte. This might indicate the formation of a few passivation products on the surface. At higher potentials, for both steel samples (immersed in the standard electrolyte and in the electrolyte containing commercial zinc-phosphate) the current increases much stronger probably indicating a general oxidation of the steel surface. This oxidation is also observed in the electrolyte containing the synthesized micro-flakes but at a higher over-potential, thus highlighting the positive effect of zinc phosphate against corrosion.

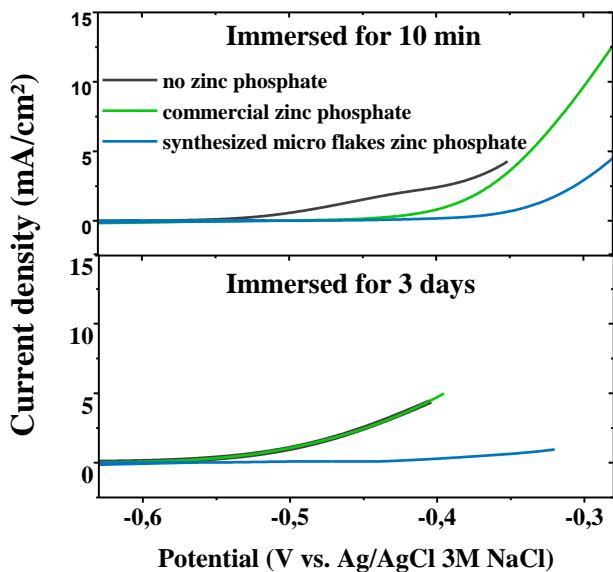


Figure 6: positive polarization of mild steel immersed in solutions containing: no zinc phosphate, commercial zinc phosphate microparticles, synthesized zinc phosphate micro flakes particles.

Polarization of the steel substrates after being immersed for 3 days in the different electrolytes also shows the passivating character of the zinc phosphate micro-flakes. Again oxidation starts at the same potential for the plates

immersed in the standard electrolyte and in the electrolyte containing the commercial zinc phosphate powders. Whereas, it requires a higher over-potential (+ 150 mV when compared to the other electrolytes) to observe a slight increase of current that would be indicative of an oxidation reaction.

3.3 Corrosion of mild steel coated with a polymeric matrix containing zinc phosphate particles

Mild steel samples coated with an epoxy-based matrix containing either commercial zinc phosphate or the synthesized micro-flakes were prepared by spin coating to highlight the importance of particles morphology in coatings. A cross section of a mild steel substrate coated with the epoxy-based film containing the zinc phosphate micro flakes is shown in Figure 7.

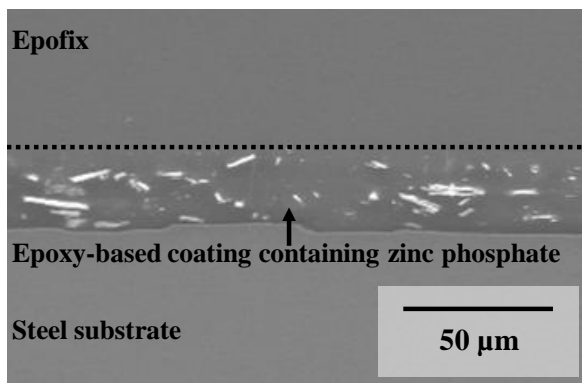


Figure 7: cross-section of a steel substrate coated with an epoxy-based coating containing 10 wt.% (solid content) of zinc phosphate micro flakes appearing in white.

The coated steel samples were immersed in a corrosive electrolyte (0.05 M H_2SO_4 + 0.5 M NaCl in H_2O). A comparison of the two samples resistances measured by electrochemical impedance spectroscopy versus their immersion time is shown in Figure 8. The higher the resistance, the higher the protective effect against general corrosion.

Both coatings present a good corrosion protection behaviour with resistance values higher than $1.10e^6$ Ohm·cm² after 90 days of immersion. However, from the first day of immersion in the electrolyte, there is a clear difference in the coating resistance, indicating a higher barrier effect for the coating containing the zinc phosphate micro flakes. This is attributed to the morphology of the flakes, as they can distribute parallel to the steel plate surface and thus increase the length of the electrolyte permeation to the steel surface.

The resistance of the coating containing the commercial particles slowly decays over the first 90 days of immersion and then shows a resistance drop associated with a visible blistering of the coating. For the sample containing the

micro-flakes, the resistance is also slightly decaying over the immersion time, but some punctual resistance increases are also observed. They are attributed to the formation of passivation products such as iron phosphate or zinc oxides/hydroxides on the steel surface. After more than 110 days of immersion, the resistance measured is more than one decade higher than the resistance of the coating containing the commercial zinc phosphate.

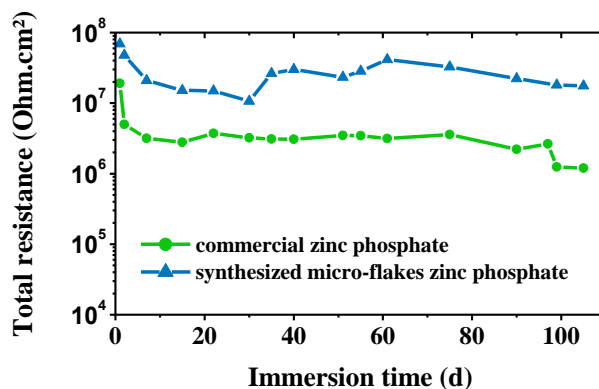


Figure 8: Evolution of the total resistance of the polymeric films containing zinc phosphate particles (commercial vs. synthesized micro-flakes) calculated from electrochemical impedance spectroscopy measurement.

4 CONCLUSION

Zinc phosphate micro-flakes were synthesized by a controlled precipitation reaction. The micro-flakes structure was obtained by the addition of an acid such as citric acid as complexing agent. The superior corrosion protection ability of the zinc phosphate micro-flakes was first confirmed by immersing mild steel samples in a NaCl electrolyte containing zinc phosphate particles. Epoxy-based films containing the synthesized micro flakes particles did also show higher performances as films containing commercial zinc phosphate, thus confirming the importance of the particles morphology.

5 REFERENCES

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