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Effect of carbon on the corrosion and wear performance of Zn-phosphate layers

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ABSTRACT

This work explains the possibility to enhance the performance of Zn-phosphate layers by the incorporation of functionalized carbon particles into the phosphating solution. The analysis focuses on both the wear behavior and the corrosion protection ability.

The study reveals that the phosphate films created with the combination of ultrasonic vibration along with the carbon particles possess a more compact structure in spite of being thinner than the conventional coatings. The analysis by electrochemistry has proved the growth of a less porous phosphate which is more rapidly developed under the novel conditions. In addition, the incorporation of the carbon particles produces analogous hopeite content, as verified by electron microscopy, an important parameter to validate the coating stability.

The reduction in the friction coefficient at the initial period of the pin-on-disk test, evidences the improved performance. The coatings prepared with carbon show enhanced wear resistance since the remaining coating after equivalent sliding distance is thicker compared to conventional coatings.

It has been demonstrated that the carbon particles play a noteworthy role in the phosphating process, as they provide additional sites for the cathodic reaction assisting to the rapid development of a more dense film.

1. Introduction

Phosphating of metals is a well-established industrial process for surface treatment, not only as temporary corrosion protection but also as pretreatment for wear resistance applications. The technological importance of these conversion coatings can be summarized as follows: corrosion protection, improvement of the adhesion of organic coatings, lubricant for deformation processes, among others [1].

The traditional phosphate process is based on a chemical conversion reaction which transforms the metallic substrate into a non-metallic crystalline coating composed by insoluble phosphate salts [1–3]. Among the multiple phosphate technologies available, those containing Zn, Fe or Mn phosphates, as well as their combinations, are the most commonly used for steel parts. A number of different formulations and procedures are available in the literature, providing a wide variety of functional requirements [1,4–7].

According to literature, Zn phosphate provides superior enhanced performance over Fe or Mn phosphates, and thus it is commonly used for long lasting corrosion protection [3–9].

From the corrosion point of view, the quality of the Zn phosphate layers greatly depends on the fraction of the total surface area covered by the phosphate coating. Several factors, such as bath composition and temperature, deposition time or incorporation of additives, affect the surface coverage efficiency. Unfortunately, most of the information about that modified phosphate technology is protected by patents and reliable references hardly appear in the scientific bibliography.

A recent work by our group included the ultrasonic vibration during the Zn phosphate deposition process, following the work published by Yang et al. concerning Mn-based coatings [10]. Our study pointed to the assistance in the nucleation step providing the development of a denser coating [11], in agreement to the above referred authors [10]. In addition, impedance spectroscopy has been successfully used as a consistent tool to study *in situ* the modifications as the phosphate coating is growing.

The incorporation of several additives in the phosphate bath, besides the common chemical accelerators, such as nitrites and nitrates, has been already considered. Some authors have

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demonstrated that additions of metal salts influence the microstructure of the final coating and make it denser and finer [12–15]. Addition of rare earth nitrates [16] or the use of triazolic compounds [17] has been pointed as suitable for the phosphate improvement as well. Mn and Nb are known to improve the corrosion resistance due to the development of a thicker coating with economic advantages and a better performance than Ni-doped phosphate coatings [12–19]. In more recent studies, SiO_2 and TiO_2 nanoparticles have been identified as providing high electrochemical stability and very good barrier protection ability [13,20].

As well as the corrosion protection ability, the wear performance is an important parameter that needs to be considered, in particular for those applications with friction requirements. The wear resistance has been the subject of numerous examinations. The majority of them concerned the advantages offered by the Mn phosphate under lubrication conditions, and only a few are related to dry friction [21–25]. Mn phosphate-based coatings decrease considerably the coefficient of sliding friction, facilitate low friction motion, eliminate scuffing and galling and reduce wear, among others benefits. By contrary, Zn phosphate, in spite of providing good barrier properties, it is not the most proper treatment to provide a suitable wear resistance on low carbon steel parts.

The aim of this work it is to modify the conventional Zn phosphate layer to offer a coating with not only an improved corrosion protection but also an enhanced wear resistance. The addition of micro sized carbon particles to the phosphating bath has been assessed. The incorporation of these particles is expected to have a catalytic effect on the cathodic reaction which could assist to the homogenization of the conversion layer improving its properties.

A recent publication used graphite grains to prepare ceramic coatings on Aluminum [26]. The fine particles with a size comparable to the layer pores could be embedded into the coating becoming it denser and less porous and thus providing a better corrosion resistance. On the other hand, graphite has been widely used as a material to modify the mechanical and tribological properties and contributes to the reduction of the friction coefficient when incorporated to different materials acting as dry lubricant [27–31]. However, regarding the phosphating technology, there is no a systematic study on the role of graphite in the microstructure of the phosphate and its correlation to the corrosion and wear resistance.

The Electrochemical Impedance Spectroscopy (EIS) technique has been used to analyze the phosphating layer. It has been proved to be a suitable method to study not only the *in situ* development of the phosphate layer [11–33], but also to provide an assessment of the coating corrosion efficiency [11,12,34].

The further surface analysis of the phosphate was completed by using Scanning Electron Microscopy (SEM). The size and shape of the crystals along with the homogeneity of the layer could be examined. The combination with the Energy Dispersive X-Ray microanalysis (EDX) and the determination of the coating weight allowed us at obtaining specific information on the phosphate composition.

The Pin-on-disk technique was performed to study the tribological properties of the phosphate coatings. The friction coefficients will be provided for both coatings with and without the incorporation of the graphite particles into the phosphating bath.

2. Experimental

2.1. Sample preparation

The chemical composition of the high strength steel rods used as the substrate for the phosphate deposition is (weight%): C, 0.81; Mn, 0.67; Si, 0.23; Cr, 0.23; Cu, 0.05; V, 0.04; Ni, 0.03; P, 0.01 and S, 0.01. Steel bars (φ = 9 mm) were cut in rods of ~15 mm height for the phosphating treatment.

Table 1
Phosphate bath characteristics.

Bath composition (100 mL)		Operating conditions	
H_3PO_4	12.5 g/L	Temperature	66 °C
ZnO	1.3 g/L	pH	2.8
$NaNO_2$	0.1 g/L	Time	6 min
$NaNO_3$	3.0 g/L		

The rod external area was hand grounded with SiC paper prior to the coating. An initial alkaline cleaning stage (in 0.1 M NaOH for 5 minutes under ultrasonic stirring) was after performed to remove the organic waste. The cleaning was completed by an acid pickling (in H_2SO_4, 180 gL^{-1}, at 52 °C for 20 minutes) to eliminate the surface rust.

2.2. Phosphating procedure

The coating treatment employed in this study is described in Table 1 following the procedure previously defined by Losch et al. [32–36]. A solution containing Ti salts was used for the prior activation step. The activation process was followed for 2 minutes, time period recently optimized to get the most protective phosphate [11].

The phosphating was chemically developed on the steel surface via immersion for 6 minutes as recommended by the sample supplier. In this stage, the application of ultrasonic (US) vibration was included in order to improve the homogeneity of the conversion layer formed as found in previous publications [10,11].

Carbon particles as graphite powder were added to the phosphating bath including the ultrasonic agitation as well. The synthetic graphite powder was supplied by Alfa Aesar® as a fine powder showing a flaky morphology. The mean particle diameter of these as-received particles is 15 μm, as measured by using the laser diffraction technique (Beckman Coulter LS I3 320).

The carbon particles must be previously functionalized in order to favor the dispersion into the phosphating solution. The amount of graphite incorporated to the bath was optimized after repetitive tests carried out with different concentrations (0.5 gL^{-1} up to 1.5 gL^{-1}). More details on the incorporation of the carbon particles, both functionalization and optimum amount, are later reported.

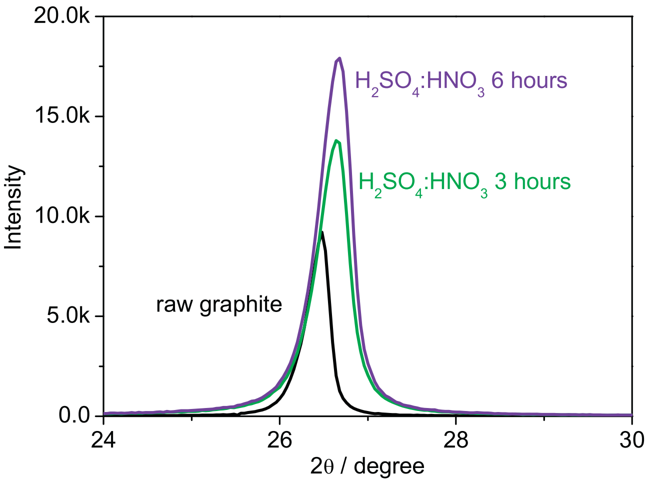

Fig. 1. X-Ray diffraction spectra of the raw graphite powder and after functionalization, for 3 and 6 hours, in 1:3HNO_3/H_2SO_4.