



Degradation and crystalline reorganization of hureaulite crystals during the manganese phosphating of a high strength steel



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ARTICLE INFO

Article history:

Received 1 December 2014

Revised 30 April 2015

Accepted in revised form 19 May 2015

Available online 22 May 2015

Keywords:

Manganese

Phosphating

Hureaulite

Degradation

Cyclic

Reorganization

ABSTRACT

This work shows that the manganese phosphating of steel is a cyclic process where crystalline reorganization is a critical stage in the development of phosphate conversion coatings. It is shown that oscillations in the manganese rich hureaulite crystal size are produced during the crystalline reorganization stage, which is related to the changes in the coating weight reported previously by various authors due to the degradation–dissolution of the crystalline layer of manganese rich hureaulite. The presence of defects (pits) in the prismatic crystals promotes their degradation due to an acidification process by differential aeration. This localized acidification process produces a composition change in the prismatic crystals that triggers a crystalline reorganization of the coating which results in a change of morphology of the hureaulite which, in turn, leads to the formation of an iron rich hureaulite inner layer. The parabolic growth of the coating may be due to the formation of this layer due to a localized attack on the steel.

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1. Introduction

Manganese phosphate coating has excellent mechanical resistance and lubricant retention properties. High coating weight and uniform crystal size distributions also result in excellent anti-galling properties and corrosion resistance. Consequently, this coating can be employed in high strength steels for the gas and oil extraction industry.

Analysis of the cross section of the manganese phosphate coating formed on steel at 90 °C reveals that the coating exhibits two layers [1,2]: a manganese rich outer layer, and an iron rich inner layer. The origin and growth characteristic of the iron-rich inner layer have not been satisfactorily explained until now and is usually referred to as an amorphous layer.

Several researchers have reported that, regardless of the chemical composition of the coating, particularly the Mn/Fe ratio, both layers exhibit the same X-ray diffraction pattern [1–4]. The coating receives the name of hureaulite due to its structural similarity with this mineral form. In the phosphating process of steel, manganese and iron can independently form the structure of hureaulite in their respective phosphating systems [5–7]. Since the manganese and iron are interchangeable in the crystal lattice of the hureaulite, the structure can be represented as: $(\text{Mn}, \text{Fe})_3(\text{PO}_4)_2 - 2(\text{Mn}, \text{Fe})\text{HPO}_4 - 4\text{H}_2\text{O}$ [8,9].

According to Bogi and McMillan [3], the total content of Mn and Fe in the structure of hureaulite is about 39–40%w, they found that the iron content depends on the concentration of this element in the bath.

These authors suggest that manganese, originally in solution, and iron, proceeding from the attack of the steel, can precipitate at the same time in different proportions during the phosphating process.

The mechanism of phosphating has been described phenomenologically by Ghali and Potvin [10] as a four stage process: 1) dissolution (attack) of the substrate in the acid medium. This stage promotes a pH increase in the bath due to the hydrogen evolution reaction (HER); 2) amorphous precipitation, involving the massive precipitation of extremely fine phosphate crystals; 3) crystallization and growth; and 4) crystalline reorganization, i.e. the phosphate in the coating dissolves and re-precipitates at a very high rate which reduces the porosity and the exposed area [10,11]. This model, proposed initially for the zinc phosphating system, has been also accepted for the manganese phosphating system and is commonly seen as a sequential process that ends at stage four.

The evolution of the coating weight has been characterized using gravimetric analysis and three sequential stages of growth are usually found: an initial linear growth, an intermediate parabolic growth and a final linear growth. The initial linear regime stage has been observed only on a few systems [1,2,12,13].

In some studies, cyclic variations of the coating weight are reported during the processing time for the various phosphating systems. These weight oscillations were first observed in zinc phosphated samples and reported in the works of Kuanishu [14] and Jimeno and Arevalo [15]. In some cases, the oscillations were considered as not significant changes, as can be seen in the work of Ghali and Potvin [10]. However, the experimental data of these researchers show oscillations in the concentration of the main elements of the coating, i.e. Zn, Fe and P.

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Furthermore, Saison [16], in a similar zinc phosphating system, found that the oscillations of the weight of the hopeite and phosphophilite phases were related to changes in the size, state and appearance of the hopeite crystals along time. He attributed this phenomenon to global changes in the phosphating solution. A similar explanation is used for zinc phosphate coatings formed under anodic galvanostatic regime when the coating weight is decreased [12]. Depending on the system used and the characteristics of the phosphating bath, these oscillations may be more noticeable as shown in the case of a CrMoV steel [17]. However, these oscillations do not alter the characteristic evolution of the coating weight previously mentioned.

The aim of this research is to generate a more accurate phosphating model that faithfully represents the experimental data available for the appearance of the substrate surface and the coating in order to improve the understanding of the several phenomena (localized attack of the steel, origin of the inner layer, parabolic growth of the coating and formation of sludge) observed during the manganese phosphating of steel.

2. Experimental

2.1. Materials

Manganese phosphating was performed on a quenched and tempered high strength steel with the following chemical composition (%w, Table 1):

Square samples of $1.5 \times 0.6 \times 0.3$ cm were used. All sample surfaces were ground on 500 grit SiC paper and rinsed with alcohol.

Phosphating solutions were prepared with analytical grade reagents and deionized water. The reagents were: manganese dioxide (99.9%w, J.T. Baker), phosphoric acid (85.8%w, J.T. Baker), nitric acid (65.7%w, J.T. Baker).

The composition of the phosphating bath was as follows: 7.95 g/L H_3PO_4 , 15.12 g/L HNO_3 and 2.085 g/L Mn. Different pH values were used: 1.1, 1.9, 2.6 (at 25 °C). Sodium hydroxide was used to adjust the pH of the bath. Phosphating of the steel samples was carried out by immersion in 50 mL of solution at 90–92 °C and pH 2.6 in an open bath from 1 to 60 min. Additional phosphating experiments were also performed at pH 1.1 and 1.9 for 5 and 20 min.

2.2. Thermodynamic analysis

Thermodynamic analysis is a powerful tool to elucidate chemical and electrochemical reactions that take place in phosphating systems and other hydrometallurgical systems. Therefore, predominance diagrams [18,19] and Pourbaix diagrams [20,21] have been constructed for several phosphating processes.

The synthetic phosphating solution contains only Mn^{2+} , H_3PO_4 and HNO_3 . However once the phosphating begins, the attack over the steel promotes the release of Fe^{2+} ions. Therefore, the phosphating process was studied thermodynamically considering that manganese and iron participate simultaneously during the process.

For the thermodynamic analysis of the phosphating system, HSC and Medusa programs were used. Both programs contain extensive databases of equilibrium constants which were complemented with the Gibbs free energy data obtained from the work of La Iglesia [22,23], to construct Pourbaix diagrams for the Fe– H_3PO_4 and Mn– H_3PO_4 systems in order to elucidate the predominance areas of the iron and manganese hureaulite.

Table 1

Chemical composition of the steel used in the phosphating tests.

Element	C	Si	Mn	Cr	Mo	Cu	S	Nb	Al	Ti	Fe
%w	0.28	0.25	0.45	1.02	0.89	0.1	0.06	0.04	0.01	0.004	Balance

2.3. Characterization

The morphology of the coatings was characterized by scanning electron microscopy using a Phillips model XL30-ESEM instrument. The chemical composition of selected areas of the coating was determined by energy dispersive X-ray spectroscopy (EDXS), using an EDAX detector (Model Genesis operated with Pegasus). Maps of characteristic X-rays were obtained to illustrate the chemical composition variations in the coating. It is worth to mention that the electron beam excites the material in the sample to a depth of $\sim 1 \mu m$ from its surface. Each point of analysis has a diameter of $1 \mu m$, so the equipment gives off an average of the point to point (local) composition in the sample. The X-ray diffraction patterns of the coatings were obtained by the powder method on a Bruker model D8 Advance diffractometer using $Cu-K_{\alpha}$ radiation. The analysis of the precipitates (sludge) formed in the bath was performed by X-ray fluorescence spectroscopy (XRF), using a Bruker model S4 Pioneer instrument.

3. Results

3.1. Thermodynamic analysis

Manganese and iron phosphates can exhibit the same structure of hureaulite [5–7] and their formation depends on the composition and temperature of the bath. The Pourbaix diagram illustrated in Fig. 1 shows that manganese hureaulite ($Mn_3(PO_4)_2$) can precipitate at pH 2.6 or higher. As shown in the same figure, the pH to precipitate iron hureaulite ($Fe_3(PO_4)_2$) is at least 0.2. The Fe– H_3PO_4 Pourbaix diagram was calculated considering that the amount of iron in the bath (from the dissolution of steel) is equal to the manganese content of the bath.

These results suggest that if the pH of the phosphating bath is below 2.6 the manganese hureaulite cannot be formed and, under these conditions, iron hureaulite would predominate in the coating. If the phosphating bath is operated at pH higher than 2.6, the manganese hureaulite would precipitate predominantly as long as Mn^{2+} ions are still present in the bath [5]. With this theoretical information, the most favorable pH bath condition was found to carry out the manganese phosphating of the steel.

3.2. Microstructural characterization of the coating obtained at low pH

Fig. 2 illustrates the typical morphology of the coatings formed at pH lower than 1.9. The samples phosphatized under these conditions exhibit the formation of a non-adherent black coating which can be observed in the sample after 30 s of immersion. The EDXS analysis (Fig. 2) indicates the presence of iron phosphates in the coating, which is in good agreement with the Pourbaix diagram of Fig. 1. It was

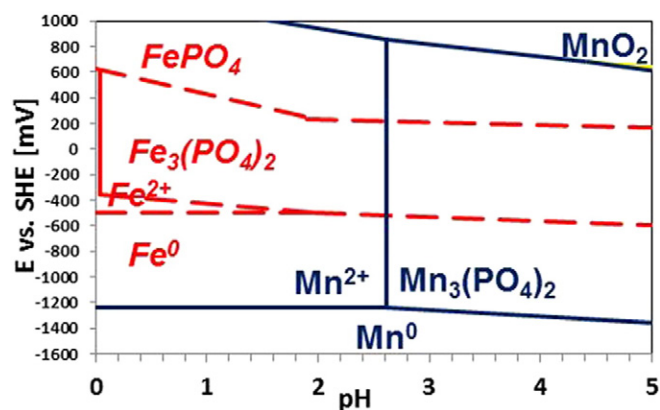


Fig. 1. Pourbaix diagram at 90 °C for the Mn– H_3PO_4 (solid lines) and Fe– H_3PO_4 (dashed lines) systems.

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