



## Full Length Article

## Deciphering the role and nature of phosphate species at the surface of stainless steel immersed in phosphoric acid solutions



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## ABSTRACT

We investigate the evolution of the surface of a highly alloyed stainless steel (Sanicro 28) upon immersion in aqueous phosphoric acid solutions. For this purpose, both short- (few hours) and long-term immersion (several days) were carried out. A detailed analysis of XPS spectra allowed a distinction to be made between oxygen originating from the organic adlayer (adventitious contamination), the passive oxide layer, and adsorbed phosphate species. By estimating the fraction of oxygen due to phosphate species ( $O_{ph}$ ), it was shown that the  $O_{ph}/P$  molar concentration ratio was ranging from about 2 to 3. This suggests the presence of a polyphosphate layer at the stainless steel surface, as also supported by Raman analysis, which influence the electrochemical behavior of SS in the acidic media.

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## 1. Introduction

Stainless steels (SS) are passive alloys extensively used in many applications involving contact with humid and aqueous media, such as in food industry [1,2], biomedical devices [3–5], structures located in natural waters [6,7], and chemical industries [8,9]. The outstanding corrosion resistance of SS is related to the formation of a nanoscale oxide layer (passive film), made of a variety of oxides/hydroxides with a complex composition, that slows down the exchange between the oxidizing species from the medium and the material bulk [10,11]. The evolution of the composition of the passive film has been the subject of a vast literature, showing its ability to “adapt” to physicochemical changes of the medium (see [12] and references therein). Since the early 1970s, electron spectroscopy has been used to probe the composition of passive films formed on SS in different conditions. In particular, X-ray photo-

electron spectroscopy (XPS) and Auger electron spectroscopy (AES) have been broadly used for that purpose, in addition to other techniques, namely secondary ion mass spectroscopy (SIMS) and ion scattering spectroscopy (ISS) [12]. An analysis of the literature showed a growing interest of using XPS for the characterization of SS surfaces compared to the other techniques mentioned above [13]. This may be explained by the performances of XPS to provide information regarding the oxidation states of alloying elements [14], and the significant development made on data exploration/treatment to identify inorganic and bio-organic compounds [15–18].

The growth and ageing of passive films in aqueous media has been reported in numerous studies [12]. In acidic media, the passivation of SS generally involves a selective dissolution of iron yielding a thin oxide layer enriched with chromium, in its trivalent state, nickel and/or molybdenum, depending on the composition of the alloy [19–22]. In these conditions, the stability of the passive film may be influenced by the presence of ions in the aqueous solutions, such as  $Cl^-$  [23],  $SO_4^{2-}$  [10,11,24,25],  $NO_3^-$  [26],  $Sn^{2+}/Sn^{4+}$  [27], etc.

In aqueous phosphoric acid media, the stability of the passive film seems to be influenced by the presence of sulfate, chloride or

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**Table 1**  
Bulk composition (wt.%) of Sanicro 28 stainless steel (UNS N-08028).

Elements	C	Mn	Si	Cr	Ni	Mo	Cu	Fe
wt.%	0.015	1.60	0.44	26.60	30.60	3.29	0.93	Balance

fluoride ions, which are common pollutants in industrial solutions. They may originate from the reaction of sulfuric acid with ground apatite phosphate rock ( $\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$ ) used in the wet process to produce phosphoric acid solutions [28]. The corrosion behavior of SS in such solutions has been investigated in few papers showing the influence of the temperature [29–33], the concentration of phosphoric acid [34,35] and aggressive ions [31]. Some authors have suggested that the corrosion resistance of SS in these conditions is due to the precipitation of phosphate species with iron or chromium originating from the passive film, thus inhibiting the dissolution of metal elements [34]. However, the identification of these compounds from XPS data is questionable, and no clear physical insights regarding the presence of iron or other metal phosphates on SS surface have been reported. In our previous work, we have suggested that the immersion of SS samples in industrial or simulated phosphoric acid solutions leads to the formation of a polyphosphate film at the surface [36]. This observation was obtained by means of Raman spectroscopy and supported by micrographs showing the presence of an insulating polymeric film.

While the electrochemical behaviour of stainless steels in phosphoric acid solutions has been already investigated by some of us [36,37] and other groups [29–35], questions about the exact mechanism of passive film changes still need to be addressed. Indeed, the nature and the fate of phosphoric species which interact with SS surfaces as well as the resulting interfacial processes have received only a little consideration. Furthermore, in these studies only short-term incubation tests (few hours) have been conducted. The aim of this paper is to investigate the evolution of the composition of passive films upon immersion of SS samples in phosphoric acid medium of industrial interest by means of XPS analysis. Both short- and long-term experiments are performed to study early stage evolution (few hours) of the passive film and its ageing for several days. The effect of the concentration of chlorides in the medium is also investigated both at room temperature (RT) and at 80 °C to assess the evolution of the passive film close to the conditions of industrial process. As complement to XPS analysis, Raman spectroscopy is also used to probe the possible presence of inorganic phases that may form on the SS surface during the immersion, and identify corrosion products that may result from the dissolution of metallic species in the acidic media.

## 2. Materials and methods

### 2.1. Stainless steel and solutions

Highly alloyed stainless steel UNS N-08028 plates ( $1 \times 1 \text{ cm}^2$ ), commercially named Sanicro 28, were used for this study. The chemical composition of Sanicro 28 SS is given in Table 1. The samples and electric contacts (copper wire) were embedded in an epoxy resin (Epofix, Struers, France) to avoid crevice corrosion during the immersion. The exposed surface was polished using SiC papers of decreasing grit size (from 120 to 2400), then thoroughly rinsed with distilled water and dried under air gas flow.

All experiments were performed in industrial phosphoric acid (IA-0.026) provided directly from the wet industrial process before its purification and includes some impurities as detailed in Table 2. The chloride concentration initially present in IA (0.026%) was increased by addition of KCl to check the effect of chloride ions on the evolution of the passive film upon immersion. The IA solutions containing an additional amount of KCl are called IA-x, where x des-

**Table 2**  
Composition of the industrial (IA) and the simplified (SIA) phosphoric acid solutions (\* KCl was added to reach concentrations ranging from 0.026 to 0.46, as indicated).

Elements	IA	SIA
$\text{P}_2\text{O}_5$	50%	50%
CaO	0.50% max	–
$\text{H}_2\text{SO}_4$	0.34%	0.34%
$\text{Fe}_2\text{O}_3$	0.50% max	–
$\text{Al}_2\text{O}_3$	1.00% max	–
MgO	1.40% max	–
F	0.45% max	–
C	600 ppm max	–
Cl	0.026%	–
M.S	0.1% max	–
KCl*	0.026–0.46%	0.026%

ignates the concentration of chlorides ( $x = 0.08; 0.13; 0.24; 0.34$  or 0.46%). Two temperatures were assessed: room temperature (RT), around 20 °C, and 80 °C which is close to the temperature found in the industrial process. As a control, some samples were incubated in pure phosphoric acid containing chloride and sulfate ions at the concentrations found in the industrial solution, named simplified industrial acid (SIA, Table 2).

The electrodes were introduced in a 250 mL open reactor without stirring and positioned vertically closed to the bottom of the electrochemical cell. SS samples were immersed for 48 h for all concentrations of chloride and further incubated up to 15, 30 or 45 days for IA-x solutions ( $x = 0.026; 0.13; 0.24$  and 0.46%). 48 h immersion were performed in a double wall open reactor maintained at 80 °C using a cryothermostat Perking-Elmer. For long time experiments, samples were placed in reactors and heated at 80 °C in an air oven. The reactors were partially open during the incubation to limit acid evaporation and totally opened to perform punctual electrochemical measurements. All chemicals used in this study were provided by Sigma-Aldrich (France) and ensured 99% minimum purity.

### 2.2. Electrochemical tests

Open circuit potential (OCP) measurements were performed using a Biologic VSP300 potentiostat (France). A saturated calomel red rod reference electrode dedicated to high temperatures was used, but the OCP values are given in the paper with respect to the saturated calomel electrode ( $E_{\text{red/rod}} = +141 \text{ mV/SHE}$  at 80 °C and  $E_{\text{red/rod}} = +194 \text{ mV/SHE}$  at 20 °C).

### 2.3. XPS analyses

XPS analyses were performed using a SPECS (Phoibos MCD 100) spectrometer (SPECS, Germany) equipped with a monochromatized Al X-ray source ( $h\nu = 1486.6 \text{ eV}$ ) and a Phoibos 100 hemispherical energy analyzer. Pass energy of 20 eV was used for the survey scan, and 10 eV for narrow scans. No charge stabilization device was used on these conductive samples. The pressure in the analysis chamber during measurement was around  $10^{-10}$  Torr. The photoelectron collection angle,  $\theta$ , between the normal to the sample surface and the analyzer axis was 0°. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, Cr 2p, Fe 2p, Ni 2p, Mo 3d, Cu 2p, P 2p, Si 2p, Cl 2s, F 1s, Na 1s, K 2p, S 2p, Ca 2p. The binding energy scale was set by fixing the C 1s component due to carbon only bound to carbon and hydrogen at 284.8 eV. The data treatment was performed with the Casa XPS software (Casa

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