Effects of oxidation-nitridation in the presence of water vapor on ASTM A335 P92 steel using SEM-EDS and XPS characterization techniques

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Abstract. This research studies the physical and chemical changes in steel ASTM A335 P92, produced from a typical refinery corrosion environment. The environment evaluated was oxidation-nitridation with the presence of water vapor. In this study five (5) exposure times were selected: 1, 20, 50, 100 and 200 hours; As well as two (2) analysis temperatures: 450 and 550°C. The working pressure used was one (1) atmosphere. Bearing in mind the kinetic study, the behaviour shown in ASTM A335 P92 steel describes an accelerated growth until 50 hours, after this time growth is less. For the tests carried out at 450°C, the kinetic constant was 2×10⁻⁸g²mm⁻⁴h⁻¹, as well as for 550°C the calculated kinetic constant was 3.1×10⁻⁷g²mm⁻⁴h⁻¹; through the SEM-EDS characterization techniques, it was possible to appreciate a good adhesion and homogeneity of the layers formed on the metal matrix until a time of exposure of 100 hours at 450 and 550°C, different from that evidenced to 200 hours of exposure where the layer formed near to the substrate showed detachment, this is attributed to the formation of hydroxides product of water vapor. Among the results obtained are the elemental composition, the presence of nitrides such as Si₃N₄, also NSiO₂ and NSi₂O, molybdenum oxides: MoO₂ and MoO₃ and iron oxides: FeO and Fe₂O₃ can be evidenced.

1. Introduction

The permanent need to maintain and improve efficiency in industrial production processes promotes the use of high temperatures, which favours the presence of more severe corrosive environments on the materials used by the different equipment. Combustion gases and water vapor represent a constant problem in equipment operating in high temperature processes, mainly due to the use of mixtures of natural gas and other streams obtained during the refining process commonly called refinery gases; a very common example is found in boiler tubes, steam generators and furnaces in the petrochemical industry [1]. When ferritic steels are subjected to high temperatures and long periods of time, failures in materials and structures begin to appear [2-5]. According to Gil, of all operational failures in industry, the most important is corrosion with 33% of cases [6]. On the other hand, it has been determined that the presence of water vapor stimulates the formation of volatile species in the form of hydroxides, stimulating the increase in the speed of corrosion of the material. One of the main reasons because the steels with nine percent of chromium (9% Cr) present such high corrosion rates in the presence of combustion gases, is due to the presence of water vapor [7-10]. In these steels, the negative effect of water vapor on oxidation is greater, as during the dry oxidation a thin layer of chromite (Cr₂O₃) is produced, which is continuous and adherent, which is a protective layer. However, in atmospheres with water vapor does not occur the formation of a layer with the same characteristics, since the water reduces...
the stability of the film of chromite, because it allows the diffusion of the atoms of Iron (Fe) through the oxide layer increasing the formation of iron oxides.

Among the alloys used in combustion equipment is steel ASTM A335 P92 (9Cr-1Mo modified), which owes its use to the aggregates of alloying elements such as tungsten (W) and boron (B) which contribute to improving mechanical properties such as creep resistance and corrosion resistance at high temperatures [11]. High temperature corrosion includes studies of the different effects that may occur according to the composition of the gas mixture: oxidation, nitridation, water vapor, among others. However, on this alloy there are few reported studies that contemplate all the aforementioned corrosive effects, and which are typical of combustion atmospheres typical of actual refining processes. For this reason, this study intends to evaluate the performance of ASTM A335 P92 steel in an atmosphere similar to those generated in the hydrocarbon combustion and transformation of a refinery furnace (oxidation-nitridation with water vapor), with temperatures on the surface between 450°C and 550°C, in order to understand the corrosive phenomena which, cause damages in this steel used in tubes for combustion processes in boilers.

2. Methodology
ASTM A335 P92 steel coupons with dimensions of 20mm×15mm×2mm were used. The coupons were machined and sanded with SiC paper from sandpaper No. 180 to 600, then cleaned in an acetone bath in ultrasound for a time of 10 minutes [11]. The tests were carried out in a tubular horizontal oven at temperatures of 450 and 550°C in an atmosphere of 79.66% N₂-1.92% O₂-18.40% H₂O (% mol), atmospheric pressure and a volumetric flow of 212.3cm³/min N₂-O₂ and 0.0358cm³/min H₂O. The selection of the study atmosphere was selected bearing in mind the study carried out at the Barrancabermeja’s refinery, in which four (4) characteristic mixtures were determined from the historical chromatographs of different refinery units [12]. The times used for each test were 1, 20, 50, 100 and 200 hours of exposure. Before and after each test the coupons were weighed on a high precision digital scale.

To understand the corrosive effects on the material, characterizations such as optical microscopy, hardness and microhardness were carried out before exposure, as well as after exposure. Scanning Electron Microscopy (SEM), a technique that allowed us to study the morphology of the layers and phases formed in the material. An elementary collective profile (Line) was also determined, as well as the punctual elemental composition in each of the phases, by means of the energy-dispersive X-Ray Spectroscopy (EDS). For the X-ray Photoelectron Spectroscopy analysis (XPS), the samples were placed on a carbon conductive belt in metal samples. In the measurements, a monochromatized Al Kα (FOCUS 500) X-ray source was used at 200W. The passing energy of the hemispherical analyser was set at 100eV for the general and 60eV spectra for high resolution spectra. The surface charge compensation was monitored with a Flood Gun (device FG 15/40-PS FG500) operated at 58μA and 2eV. Finally, the hardness tests were performed with a Rockwell A hardness tester and microhardness with the digital microdurometer in Vickers respectively.

3. Results
Initially, a metallographic characterization of ASTM A335 P92 steel was performed to determine microstructural changes. In Figure 1(a), the initial microstructure composed of a ferritic matrix with a martensitic structure is observed. Figures 1(b) and (c) show the microstructures after exposure to the atmosphere at 450 and 550°C respectively, where the steel presented atomic diffusion by heating generating precipitation of carbides of tungsten, chromium, molybdenum and manganese among others. It was possible to show the precipitation of carbides and a martensite structure.

In the Table 1 shows the chemical composition of the study material, this analysis carried out in SMT Laboratorio Prove Tecnologiche ed Analisi (Tenaris).
By means of the SEM technique, the formation of three homogeneous layers on the surface of the steel P92 after a time of exposure to 100 hours in the atmosphere O2-N2-H2O at 450 and 550°C could be evidenced. According to what was reported in the literature, in addition to the XPS technique, the outer layer corresponded to hematite (Fe₂O₃), the intermediate layer to Magnetite (Fe₃O₄), and the inner layer corresponded to a spinel of chromium and iron [13]. It was observed that the inner layer has a homogeneous structure for both working temperatures. The presence of voids in the interface of the outer layer and the intermediate layer is observed, allowing signs of detachment of the layers from one to another. The hydroxides generally have greater volatility than the corresponding oxide, and this leads to loss in the protection of the material. Thus, the rapid diffusion of water into oxides is possible because by variation of protons located in the oxide ions that move by transferring one oxygen to another. Because the concentration of OH⁻ ions is high, allow the formation of compounds with cationic vacancies, and this in part is responsible for the observed increase in corrosion rates (Figure 2).
On the other hand, using the EDS analysis the determination of the elemental composition of three points in each layer formed after a time of exposure to 100 hours at 450°C was carried out. Through of this technique it was possible to identify the elements present in the layers formed on the surface (Figure 3).

Through the images of the outer layer in contact with the atmosphere and the intermediate layer, it is possible to observe the high percentage in the iron and oxygen elements, characteristic of the oxides referred to above according to the SEM characterization technique; in the inner layer in contact with the base metal it is possible to observe a higher concentration of the chromium element in comparison to the other two layers.

Figure 2. Layers formed on the surface of P92 after exposure to the O$_2$-N$_2$-H$_2$O environment for 100 hours (a) 450°C and (b) 550°C.
Figure 3. EDS of P92 steel at 100 hours and 450°C. (a) outer layer (b) intermediate layer and (c) inner layer in contact with the base metal.

With X-ray Photoelectron Spectroscopy (XPS) technique, it was possible to determine the elemental surface composition and the products formed, from the chemical properties of the elements. The analysed elements were chosen bearing in mind the composition of the steel and the corrosive environment. Table 2 shows the percentages by weight of the elements present.

Table 2. Elemental percentage at 100 hours, 450 and 550°C.

| Element | 450°C (%w) | 550°C (%w) |
|---------|------------|------------|
| O       | 25.446     | 22.799     |
| Cr      | 2.4670     | 4.7805     |
| N       | 0.6038     | 0.05850    |
| Mo      | 1.4999     | 4.4601     |
| Fe      | 32.666     | 30.599     |

It is verified the presence in greater proportion of elements like oxygen, chromium, and iron. On the other hand, bearing in mind that the steel studied contains 0.039% by weight of the initial elemental composition, the increase in the weight percentage of the nitrogen content in the surface is corroborated.

Regarding the electronic information and the products formed after the exposure to the corrosive environment, the following results were presented bearing in mind the XPS Handbook [14] and the program (simplified) containing the equipment software: Oxygen: It was found with atomic level 1s and according to the binding energy was determined the presence of metal oxides, SiO$_2$, and Al$_2$O$_3$. On the other hand, from the metal oxides, the binding energy of O$_1$ of many compounds and species is within a very narrow range. Thus, O$_1$ peaks tend to be wide, with multiple components superimposed and components due to water and/or organic contamination overlap directly with SiO$_2$, for example. Nitrogen: The atomic level is 1s and according to the binding energy was determined the presence of metal nitride Si$_3$N$_4$ and compounds like NSi$_2$O and NSiO$_2$. Chromo: The atomic level is 2p and strongly overlaps with Auger of Zn LMM peaks, which is very frequent in samples of steels. In the presence of high concentrations of zinc, it may be difficult to assign the chemical energy of the chromium using the Cr 2p region, due to the strong overlap with the Zn LMM Auger region. The Cr 2p peak has spin-orbit components. Thus, the presence of metallic chromium could be determined, but not the oxides present.
in P92 steel. Molybdenum: The atomic level is 2s and the presence of metal Mo, MoO₂ and MoO₃ is evidenced. Iron: The atomic level is 2p and tends to overlap strongly with Auger Ni LMM line peaks. Iron metal, FeO and Fe₂O₃ are present.

Also, the kinetic study was carried out by means of the analysis of the curves obtained of the variation of the mass as a function of the time of exposure to the working temperatures. The data recorded to determine the corrosion rate were expressed as mass gain per unit area (g/mm²). The curves show a clear parabolic tendency up to 50 hours of exposure for both temperatures, after this time the steel has a mainly protective characteristic, attributed to the stabilization of solids by means of the alloying elements such as tungsten, vanadium, among others (Figure 4). Based on non-linear regressions, it was possible to establish the speed laws for the two working temperatures. These can be seen in Table 3.

The kinetic constants obtained are lower than those reported by Ehlers at 650°C, as expected, for a similar oxidizing environment, composed of N₂-1% volO₂- (2-7% vol) H₂O [15].

![Figure 4. Exposure time vs mass gain of P92 steel at 450 and 550°C.](image)

| Work temperature (°C) | Speed law | Kinetic constants (g² mm⁻⁴ h⁻¹) | Percentage error |
|-----------------------|-----------|-----------------------------------|-------------------|
| 450                   | $x^2 = 2.037 \times 10^{-8} t + 3 \times 10^{-6}$ | 2.037x10⁻⁰⁸       | 2.6380x10⁻⁰⁶     |
| 550                   | $x^2 = 2.77 \times 10^{-07} t + 2 \times 10^{-05}$ | 2.77x10⁻⁰⁷        | 2.806x10⁻⁰⁵      |

4. Conclusions
Metallographic analyses showed changes in the steel microstructure, indicating the presence of carbide precipitation at the grain boundaries and a martensitic structure with thinner needles. On the other hand, the formation of protective oxide layers was evidenced on the surface of the material, which maintains in good condition the properties in service of this steel at these temperatures and working time. The results obtained from SEM-EDS and XPS characterization techniques showed congruence between the corrosion products identified in the P92 steel, among which are nitrides, and oxides, finally, the kinetics of the oxidation-nitriding process showed a behaviour with an accelerated growth until 50 hours, then the variation was less; also, was possible evidence the direct relationship between the corrosion rate and the temperature in the two kinetic constants found for 450 and 550 °C.

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References
[1] Alvarez E and Infazon D 2009 Oxidación isotérmica y cíclica del acero ASTM A335 P92 a alta temperatura (Bucaramanga: Universidad Industrial de Santander)
[2] Van Wortel J C, Etienne C F and Arav F 1992 Application of modified 9chromium steels in power generation components Conference Proceedings The manufacture and properties of steel 91 for the power plant and process industries: ECSC Information Day, (Dusseldorf) (Germany: TIB) paper 4.2
[3] Fujita T 1992 Current progress in advanced high Cr steel for high temperature applications ISIJ International 32(2) 175.
[4] Birchenall G E 1981 A brief history of the study of oxidation of metals and alloys High Temperature Corrosion Proceedings (USA: Nace) p 3
[5] Jones D A 1996 Principles and prevention of corrosion second edition (USA: Prentice Hall)
[6] Gil L 2013 Corrosión en la industria del petróleo y el uso de tecnologías de recubrimientos como alternativa de protección Memorias del Segundo Encuentro Internacional de Investigadores en Materiales y Tecnología del Plasma (Bucaramanga: Universidad Pontificia Bolivariana) p 24
[7] Khanna A S, Rodriguez P and Gnanamoorthy J B 1986 Oxid. Met. 26 171-200
[8] Fujii C T, Meussner R A and J. Electrochem 1963 Soc. 110 1195-1204
[9] Pujilaksono B, Jonsson T, Halvarsson M, Svensson J and Johansson L 2010 Corros. Sci. 52 1560–1569
[10] Birks N and Arnold E 1983 Introduction to high temperature oxidation of metals (London: Edward Arnold Publishers Ltd)
[11] ASTM G1-03 2011 Metals Standard practice for preparing, cleaning, and evaluating corrosion test specimens (USA: ASTM International)
[12] Cala O M, Merriño L, Kafarov V and Saavedra J 2013 Efecto de la composición del gas de refinería sobre las características del proceso de combustión Rev. Ingenierías Universidad de Medellín 12(23) 101-112
[13] Serna J 2003 Oxidación, carburación y sulfidación de aleaciones ferríticas Fe-9Cr-1Mo modificadas en ambientes con hidrocarburos a temperaturas entre 550 y 750°C (Bucaramanga: Universidad Industrial de Santander)
[14] Moulder J 1992 Handbook of X-ray photoelectron spectroscopy: A reference book of standard spectra for identification and interpretation of XPS data ed Jill Chastain, Roger C. King (USA: Physical Electronics) p 43-49
[15] Ehlers J et al 2006 Enhanced oxidation of the 9%Cr steel P91 in water vapour containing environments Corros. Sci. 48(11) 3428–3454.