Study of the continuous corrosion in an oxidation environment derived from the theoretical combustion products in a refinery. Case study: Ferritic steel ASTM A335 P91

To cite this article: A Alviz Meza et al 2017 J. Phys.: Conf. Ser. 935 012057

View the article online for updates and enhancements.

Related content
- The Cross-Sectional Investigation of Oxide Scale FeCr Alloys and Commercial Ferritic Steel Implanted with Lanthanum and Titanium Dopants after Oxidation Test at 800°C 
  Hendi Saryanto, Darwin Sebayang, Pudji Untoro et al.
- Comparison of rolling texture of austenite and ferrite phases of duplex steel with single-phase austenitic and ferritic steel 
  J Capek, M Cernik, N Ganev et al.
- The influence of carbide coarsening on the friction properties of thermally affected 9–12 wt. % Cr steels 
  I. Velkavrh, F. Kafexhiu, S. Klien et al.

IOP ebooks™
Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.
Start exploring the collection - download the first chapter of every title for free.

This content was downloaded from IP address 207.241.231.81 on 26/07/2018 at 06:44
Study of the continuous corrosion in an oxidation environment derived from the theoretical combustion products in a refinery. Case study: Ferritic steel ASTM A335 P91

A Alviz Meza¹, V Kafarov¹ and D Y Peña Ballesteros¹
¹ Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: anibalalvizm@hotmail.com

Abstract. Corrosion studies are key element that ensure the correct functioning of equipment in the industrial sector. The oxidation phenomena were evaluated, taking as a case study steel ASTM A335 P91 (P91), a steel of typical use in equipment that work at high temperatures. Five (5) exposure times were selected for the experimental development: 1, 20, 50, 100 and 200h; as well as four (4) analysis temperatures: 450, 550, 650 and 750°C. Through the metallographic analysis was possible to evidence the presence of multiple carbide precipitates and a ferritic structure, after all the temperatures tested. On the other hand, the analysis of hardness and microhardness showed an increase for all the evaluated temperatures. These increases were mainly related to the precipitation of carbides in the coupons of P91. Regarding to the chemical analysis, it was possible to conclude that after 200h of experimentation in each temperature, a layer of duplex oxide, composed mainly of hematite, magnetite and spinel iron-chromium, was formed in the O₂/H₂O atmosphere. Finally, the kinetic study demonstrated that the oxide layer formed on each coupon of P91 was of protective character.

1. Introduction

The most important reaction in the processes developed at high temperatures is oxidation, being that when the oxide layers formed are protective, other types of corrosion can be prevented, as is the case of internal corrosion. However, not all oxide layers formed are protective; in the absence of water vapour a protective chromium-rich spinel scale is developed, but upon introduction of water vapor breakaway oxidation occurs [1,2].

The oxidation behaviour of Cr-Mo steels in water vapor, supercritical water, air and pure oxygen has been extensively studied [3–11]. When there is presence of water vapor, it has been extensively reported that the oxide layer formed is constituted by a duplex structure; composed of Fe and Cr oxides (Fe₂O₃, Fe₃O₄ and Fe₃-xCrₓO₄, Cr₂O₃, FeO). The outer layer is predominantly in iron oxides, while the innermost layer contains a significant amount of chromium. In addition, the effect of the water vapor has a disruptive effect on the oxide layers, generating the formation of volatile oxides such as: Cr(g), CrO₃(g), CrOOH(g), CrO₂(OH)₂(g), Cr₄OH(g), FeOH(g), FeO(g), Fe₉₆O₉(g), Fe₃O₅(g), which generate voids, pores, cracks and detachment of oxide layers, facilitating the damage by other forms of corrosion [12].

However, although that the oxidation process on ASTM A335 P91 (P91) steel has been extensively studied, there is little information on how this phenomenon occurs under simulated combustion conditions in a refinery.
2. Methodology
The methodology selected to evaluate the HTC on P91 steel was divided into a simulation part and an experimental part, as follows in the next sections.

2.1. Simulation methodology
The simulation in this study required the selection of a mixture model of RG from a furnace of Barrancabermeja’s refinery; it was done through the statistical study of the most representative compounds found in the historical chromatography’s records. With the RG mixture were obtained the theoretical combustion products (TCP) in Aspen HYSYS 8.6, which were used in HSC chemistry 5.11 to obtain the theoretical corrosion products (TCOP). The procedure is shown in the Figure 1.

![Figure 1. Methodology for the simulation of theoretical corrosion products.](image)

2.2. Experimental methodology
For the experimental development, the installation of corrosion coupons of P91 steel in the furnaces from the experimental scheme shown in Figure 2 was realized. The dimensions selected for each coupon were $15 \times 10 \times 2$ mm (height $\times$ length $\times$ Width), with enough area to get appreciable mass gain.

As is shown in Figure 2, to complete the required mixture of $O_2/H_2O$, the humidification of the $O_2$ gas was performed through the use of a bubbler. This bubbler was initially calibrated at the appropriate temperature, in order to obtain the simulated molar composition of the TCP in the furnaces.

![Figure 2. Experimental setup, where: (1) Cylinder with $O_2$, (2) Cylinder with Air, (3) Flow valve, (4) Mass flow meter, (5) Flow regulator, (6) Humidifier, (7) Pressure gauge, (8) Heating cord, (9) Horizontal tubular electric furnace, (10) Relief valve, (11) Gas and steam outlet.](image)

With regard to the preparation of the coupons; the coupons were sanded before testing with silicon carbide paper, until reaching the sandpaper 600 on all the sides. Each coupon was subjected to ultrasonic cleaning in acetone, dried and marked, as is recommended by standard ASTM G1. The coupons were characterized by the following techniques: SEM-EDS, XRD, hardness, microhardness and optical microscopy. In addition, the kinetic study was carried out taking into account the dimensions of the coupons, as well as the mass gained by each one in the different times of exposure. The complete experimental methodology is shown in the Figure 3.

![Figure 3. Methodology for the experimental development.](image)
3. Results and discussion
It is important to mention that the temperature in this study was selected according to a thermography taken from the radiation zone of a furnace from Barrancabermeja’s refinery. So, the temperature in this work was selected between 450 and 750°C.

3.1. Determination of combustion products and gas mixture
The selection of the RG model mixture was made based on the average of the compounds of higher occurrence in a chromatographic study of a refinery furnace [13]. The Table 1 shows the composition.

| Compounds | CH₄ | C₂H₆ | C₄H₁₀ | C₂H₄ | C₃H₆ | H₂S | H₂ |
|-----------|-----|------|-------|------|------|-----|-----|
| %Molar    | 55  | 10   | 4     | 5    | 2    | 4   | 20  |

The TCP were determined for a 10% of air in excess in an adiabatic combustion furnace simulated in Aspen HYSYS 8.6. The TCP are shown in Table 2.

| Compounds | CO₂ | O₂  | N₂   | H₂S | H₂O |
|-----------|-----|-----|------|-----|-----|
| % Molar   | 9.10| 1.74| 72.15| 0.34| 16.67|

Starting from the molar ratio of the TCP, the molar composition of the O₂/H₂O sub-mixture was obtained (Table 3).

| Compounds | O₂   | H₂O |
|-----------|------|-----|
| % Molar   | 9.47 | 90.53|

Finally, to obtain the flows used, a mass flow of 333.4mg/min was assumed for the complete mixture of the TCP. Thus, with the physical properties of the gases at 298.15K, a volumetric flow of 5.01cm³/min for the O₂ gas and 35.83mg/min for the mass flow of water vapor in the humidifier were calculated.

3.2. Theoretical combustion products
By using the HSC Chemistry program and the phase stability diagram, theoretical potential corrosion products were established between 450 and 550°C, for one atmosphere of pressure. The molar ratio used between steel and gas was 1/1000 as is recommended in other studies [14]. The Table 4 shows the composition of the P91 steel.

| %Mo | %C | %Si | %Mn | %P | %S | %Ni | %Cr | %V | %Nb | %Al | %N | %Fe |
|-----|----|-----|------|----|----|-----|-----|----|-----|-----|----|-----|
| 0.989 | 0.106 | 0.768 | 0.316 | 0.013 | 0.003 | 0.271 | 8.439 | 0.024 | 0.008 | 0.006 | 0.015 | 88.807 |

Among the corrosion products found on the P91 steel for all the temperatures tested, mainly oxides were obtained: hematite (Fe₂O₃), magnetite (Fe₃O₄), wplustita (Fe₁₄O₃), chromium oxide (Cr₂O₃), silicon oxide (SiO₂), molybdenum oxide (MoO₃), manganese oxide (MnO₂), CrO₂, FeOOH and spinels of Cr and Mn (FeCr₂O₄ and Fe₃MnO₄). On the other hand, using the phase stability diagram between 450 and 750°C, it was showed that is thermodynamically feasible the stabilization of iron oxide (FeO) and chromium oxide (Cr₂O₃) on P91 steel in an atmosphere of O₂/H₂O, as shows the dot in Figure 4.
4. Experimental results
The results of the physical and chemical analysis performed, in addition to the kinetic study, are presented as follows.

4.1. Metallographic analysis
In Figure 5(a), it is possible to observe fine grained, martensitic structure, with homogeneous distribution of precipitates in the matrix, characteristic behavior of normalized and tempered P91 steels. Additionally, the increase of elongated and rounded carbides could be noted with the increase in temperature (Figure 5(b)).

![Figure 5. Optical microscopy (500X) for P91 steel: (a) before exposition and (b) after 200h of exposition at 750ºC.](image)

4.2. Analysis of hardness and microhardness
The hardness analysis on all coupons exposed for each temperature and time did not show any significant changes. This leads to the conclusion that the material did not suffer substantial structural changes during the tests, as the metallographic analysis showed. On the other hand, the microhardness analysis showed an increase in all the cases, which was related to the appearance of multiple carbides at each exposure temperature (Table 5).

|                  | Initial state | 450°C | 550°C | 650°C | 750°C |
|------------------|---------------|-------|-------|-------|-------|
| Hardness (Rockwell A) | 47.00         | 47.65 | 47.20 | 49.64 | 49.80 |
| Microhardness (Vickers HV) | 229.40       | 244.05| 243.48| 288.40| 255.40|

Table 5. Analysis of hardness and microhardness after 200 h of test in all the temperatures evaluated. The force applied by each analysis was respectively 588.40 and 0.49N.
4.3. Scanning electron microscopy with x ray microanalysis

Through this study, it was possible to observe the morphology of the oxide layers deposited on P91 steel. In addition, from the EDS analysis it was identified the elemental profile of the different oxide layers. In Figure 6, two layers of oxides can be observed for all the temperatures studied, after 200h of exposure to the $O_2/H_2O$ atmosphere. As has been reported extensively in other oxidation studies on P91 steel, these two oxide layers correspond to: an outer layer of hematite and magnetite and an internal, which is the thickest, composed mainly by an iron-chromium spinel. This latter only of protective behaviour at 450 and 550°C. Additionally, the presence of cracks, pores and voids in the outermost layers can be observed, so it is also suggested the formation of volatile oxides, a characteristic behaviour during the phenomenon of breakaway oxidation on P91 steel. Finally, a depletion of the alloying elements in the metal interface is also observed, an effect that became more severe with the increase in temperature.

![Figure 6. SEM for coupons of P91 exposed to 200h at: (a) 450°C (5000X), (b) 550°C (2000X), (c) 650°C (500X), (d) 750°C (250X).](image)

Regarding the oxidation mechanism, it is possible to take into account the explanation given by Quadakkers et al. [3]: The breakdown of the protective spinel scale is accompanied by formation of a rapidly growing magnetite layer and an inner scale consisting of $Cr_2O_3$ precipitates in a “FeO-matrix”. Then the separation of the oxide layers is due to the appearance of multiple vacancies in the spinel layer, which promotes the formation of the magnetite layer. Further the corrosion mechanism depends of the "$O_2/H_2O$ bridges", which are in charge of the transport processes between the voids, as is suggested by Rahmel and Tobolski [15]. Finally, due to the formation of large voids, diffusion of the Fe atoms between the layers is difficult, resulting in a layer of hematite, which is an oxide in equilibrium with the surrounding environment. From that point, the growth of the oxide layers is largely temperature dependent.

Otherwise, in Figure 7 the presence of the three oxide layers formed on P91 coupons, are evident when the fluctuations between chromium, iron and oxygen are monitored. In addition, Mn, Si and Mo are present mostly in the innermost oxide layer.
4.4. X-ray diffraction analysis
Through the conventional X-ray diffraction analysis, it was identified the compounds formed on the surface of P91 steel. The presence of magnetite (Fe₃O₄) and hematite (Fe₂O₃) were confirmed. However, considering the results of EDS, the formation of chromium-rich spinels in the inner oxide layers is not ruled out, nor is the presence of other oxides.

4.5. Kinetic study
The behavior of the graphs in Figure 8 is close to parabolic, which suggests the presence of layers of protective oxides, where the diffusive processes decrease with time. The results obtained through the analysis of SEM support the presence of a protective internal oxide layer, composed mainly of iron-chromium spinel.

![Figure 7. SEM-EDS for coupons of P91 exposed to 200h at 750°C (250X). The elemental concentration increases from left to right in each box.](image)

![Figure 8. Thickness of the oxide layer against time for each study temperature.](image)

The kinetic constants showed a clear increase in the oxidation rate at 650 and 750°C, compared to 450 and 550°C (Figure 6). Finally, is possible to say that the relationship between the oxidation kinetics and the temperatures used, was not linear but rather quadratic for P91 steel (Table 6).

| Table 6. Kinetic constants for temperatures tested. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Kinetic constants (mg² * mm⁻⁴ * h⁻¹) | 450°C           | 550°C           | 650°C           | 750°C           |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| 3.30x10⁻⁷                      | 5.12x10⁻⁶       | 2.07x10⁻⁴       | 6.41x10⁻⁴       |
5. Conclusions

Coupons of P91 were exposed to an oxidation environment obtained from a model refinery mixture and the molar ratios of its theoretical combustion products. It was found that there was congruence between the experimental and simulations results; where the compounds reported by EDS and XDR analysis showed the presence of external oxide layers rich in iron and inner layers rich in chromium. Also, the phenomenon of breakaway oxidation between the inner and outer layers was presented, revealing the weak protective character of iron oxide layers in wet environments. These results are similar to those reported by several researchers in wet environments, information very well compiled by Saunders et al. [7]. These conclusions, were supported by kinetic analysis, where parabolic behavior was evidenced in the mass gain graphs; noting that the oxidation kinetic constants presented a quadratic relation with the increase in temperature. further, the hardness and microhardness analysis showed respectively no substantial changes and a slight increase. This behavior suggests small changes in the structure of the material and the presence of multiple precipitates of carbides, as was corroborated in the ferritic structure of P91 steel using the optical microscopy.

Acknowledgments

The authors want to give thanks to “Universidad Industrial de Santander, Decanatura de la Facultad de Ingeniería Fisicoquímicas, Centro de Investigación para el Desarrollo Sostenible en Industria y Energía and Grupo de Investigaciones en Corrosión”.

References

[1] Young D J 2008 High Temperature Oxidation and Corrosion of Metals vol 2 (Amsterdam: Elsevier) pp 539-589
[2] Lai G Y 2007 High Temperature Corrosion and Materials Applications vol 1 (USA: ASM International) pp 5-62
[3] Ennis P J and Quadakkers W J 2008 Creep-Resistant Steels 19 519–535
[4] Ehlers J, Young D Y, Smaardijk E J, Tyagi A K, Penkalla H L, Singheiser L and Quadakkers W J 2006 Corrosion Science 48 3428–3454
[5] Laverde D, Gómez-Acebo T and Castro F 2004 Corrosion Science 46 613–631
[6] Swaminathan S, Mallika C, Krishna N G, Thinaharan C, Jayakumar T and Mudali U K Corrosion Science 79 59–68
[7] Saunders S R J, Monteiro M and Rizzo F 2008 Prog. Mater. Sci. 53 pp 775–837
[8] Ostwald C and Grabke H J 2004 Corros. Sci 46 1113–1127
[9] Zurek J, Wessel E, Niewolak L, Schmitz F, Kern T U, Singheiser L and Quadakkers W J 2004 Corros. Sci. 46 2301–2317
[10] Castaño S I, Bolivar F J and Perez F J 2010 Oxid. Met. 74 61–78
[11] Martinelli L, Desgranges C, Rouillard F, Ginestar K, Tabarant M and Rousseau K 2015 Corrosion Science 100 1–29
[12] Perez F J and Castaño S I 2006 Oxid. Met. 66 231–251
[13] Cala O M, Kafarov V and Saavedra J 2013 Rev. Ing. Universidad de Medellín 12(23) 101–111
[14] John R 2010 Sulfidation and mixed gas corrosion of alloys Shreir's Corrosion vol 1, ed Tony J.A. Richardson (Amsterdam: Elsevier B. V.) p 247
[15] Rahmel A and Tobolski J 1965 Corros. Sci. 5(5) 333–346