Yttrium oxide evaluation as coating to reduce the corrosion velocity in industrial equipment working under combustion environments. Case study: Ferritic 9Cr-1Mo steel

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Abstract. The well-known scientific problem about global warming and less cost energy requirement, has been boosting to the petrochemical sector to implement eco-efficiency strategies by promoting the use of critical conditions throughout the traditional chain process of oil refining. In addition, many industrial combustion processes are developed using as energy source a mixture of natural and recovery gases, which added to high temperatures generate potential corrosion atmospheres. Thus, this research aims to try to reduce the pipeline degradation that take place in combustion environments by evaluating an yttrium oxide as coating for the ferritic 9Cr-1Mo steel. This coating was deposited on the substrate by plasma laser deposition, and several growth times were implemented to evaluate its thickness effect. On the other hand, in order to obtain the real combustion atmosphere, a flue gas model composition was selected, which was useful to calculate the theoretical oxidation products by simulation. Finally, those coatings were evaluated at 650 °C and testing times from 1 hour to 100 hours inside the calculated oxidation environment. The main results indicated that even with the tested coatings, the evaluated alloy had a severe corrosion velocity, but lower than without them.

1. Introduction
9Cr-1Mo ferritic (P91) steel is one of the most commonly used alloys in high temperature processes developed in the oil refining industry, however, under the effect of water vapor it faces high corrosion rates [1,2]. In wet environments, this steel generates an oxide of duplex structure [1–7], which does not constitute a protective layer against cations and anions migration. Thus, it was tried to find a better steel response by implementing a highly reactive oxidation coating. The reactive element oxides (REOs) are one of the coating families most studied for this purpose on ferritic steels, therefore, they are frequently applied in SOFC cells [8]. Besides, the yttrium oxide has been proven successfully in ferritic steels at high temperatures, reducing their corrosion rate by forming perovskites rich in Cr [9].
Furthermore, most experimental observations have indicated that small amounts of reactive elements, or their oxides in the form of dispersed particles, effectively reduces the mass transfer processes at high temperature and greatly improves the layers’ adhesion [10]. The passivation mechanism established for these coatings includes: the REO’s migration through the oxide grain boundaries, the segregation around them and the blocking of the diffusion routes typically used by P91 cations. Then, the cations diffusion to the gas interface is inhibited, preventing the injection of vacancies at the metallic boundary and consequently the nucleation of these empty spaces [11]. Based on this last argument, the pulsed laser deposition (PLD) technique was selected in this work; since, it takes advantage of the benefits granted by the high vacuum for the growth of little porous, homogeneous and compact films.

Considering this, the objective of this study was focused on the evaluation of a promising coating of the REOs family, yttrium oxide, as an alternative to reduce the high degradation rate of ferritic 9Cr-1Mo steel in steam; conditions under which the Colombian petrochemical industry actually works.

2. Materials and methods
The methodology used to achieve the proposed objective was divided in two sections: coating preparation/deposition and oxidation tests.

2.1. Coating preparation and deposition
About 0.91 g of yttrium were used to obtain the Y$_2$O$_3$ target, then, two drops of polyvinyl acetate were added to agglutinate the powder for 10 min. Next, the resulted mixture was pressurized in a reflex powder compaction equipment, by applying a load of 7 tons to the 13 mm die where it was placed. This process lasted 5 min, after which the applied load was slowly decreased at a rate of 1 ton/min, to prevent the yttrium target breaking.

Continuing with the sintering process, the heat treatment of the target was conducted as follows: first a ramp of 1 °C/min until reaching 300 °C, this temperature was holderd for 1 h, second a ramp of 5 °C/min until reaching 1200 °C, remaining this way for 12 h, and finally a cooling at the same rate. The final target’s dimensions were: a diameter of 13 mm and a thickness of 3 mm, with a white appearance.

The variable to be controlled during the equipment calibration was the yttrium film growth rate. Other variables considered were frequency, power and the focal lens point. Additionally, the motor trajectory calibration was performed in the two sweep target dimensions. The optimal values found were: a scanning area of 8mm x 8mm, a frequency of 7.5 Hz and a power of 80 mW, for a wavelength of 266 nm. The distance between substrate and target inside the equipment was taken as close as possible, about 6 cm, for a perpendicular layout between target and substrate.

At last, the vacuum under which the deposits grew fluctuated between $10^{-10}$ and $10^{-11}$ atm. Figure 1 illustrate how the PLD system was set up.

![Illustrated PLD system](image)

**Figure 1.** Illustrated PLD system [12].

The growth film times evaluated were 4 h, 6 h, 8 h, 10 h and 12 h (but only 4 h, 8 h and 12 h coatings were selected for oxidation tests), to later determine their thickness through the atomic force microscopy
(AFM) analysis. This technique helps to know the layers thickness by creating an area on the substrate in which the coating deposition is not allowed. Moreover, the yttrium oxide layer obtained in each case was characterized by X-ray photoelectron spectroscopy (XPS) in situ. For this, a monochromatic Al-kα X-ray source operated at 100 W was used. The spectrometer pass energy was fixed at 20 eV, and the estimated overall instrumental broadening was 0.75 eV. Furthermore, the background pressure during data acquisition was 10⁻¹² atm. Thereby, the regions studied were: O 1s, Fe 2p, Cr 2p and Y 3d, setting the adventitious carbon peak at 284.8 eV.

2.2. Samples preparation and experimental oxidation setup
The dimensions selected for the evaluated P91 steel samples were 15 mm high x 10 mm long x 2 mm wide, which were obtained through the wire cutting technique.

The surface of the steel was prepared with SiC abrasive paper, with the following grain sizes: 180, 320, 400 and 600, until achieving fine finishes. Subsequently, the coupons were degreased and decontaminated by ultrasonic bath in acetone for 10 min. At the end, the samples were dried and weighed before being coated with yttrium oxide. All the previous preparations were carried out following the ASTM G1-03 standard [13].

Figure 2 shows the experimental setup, as described below. At the beginning, the design allowed to choose between the volumetric flow of argon and oxygen, depending on whether it was desired to start a reaction or not. Regularly, the argon was used before and after the corrosion tests, while the oxygen volumetric flow was controlled and measured through a digital flowmeter system, to be then humidified in a bubbler. Because of the above, heating cords were used to bring the steam to the electric furnace, avoiding its condensation.

The oxidizing gases and its molar composition were obtained as is suggested by Alviz, et al. [7] where, starting from a refinery model mixture and its theoretical combustion gases, an approximate molar ratio of 1/10 was obtained for the mixture O₂/ H₂O. Also, the volumetric flow of oxygen was 5.01 ml/min and the mass flow of water 35 mg/min.

![Figure 2. Experimental setup, where: 1) Ar cylinder, 2) O₂ cylinder, 3) flow valve, 4) relief valve, 5) pressure regulator, 6) digital flow meter, 7) bubbler, 8) humidifier temperature control, 9) heating cord, 10) horizontal tubular electric furnace, 11) samples, 12) furnace control temperature, 13) sample holder and 14) residual gases outlet.](image)

After the oxidation tests, X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS) were carried out to obtain information about the crystalline phases and the layer morphology, respectively. For the conventional XRD analysis, the record range used was between 3.5 °2Theta and 70 °2Theta.
Meanwhile, the kinetic study was performed by mass gain and layers thicknesses (revised by means of SEM) analysis. For the SEM technique, the samples cross section preparation as suggested by the ASTM E3-95 standard [14] was conducted. Nevertheless, the thickness analysis helped to calculate the P91 corrosion rate severity in accordance with the NACE RP0775-2005 standard [15].

Finally, the total number of tests was 15, as a result of the combination of five times and three coating thicknesses, corresponding to a standard factorial design.

3. Results and discussion

3.1. Coatings characterization

As it’s shown in Figure 3a, the coating growth was proporsional to the target erosion time, giving an average growth rate of 56.6 nm/h. Further, the deposition time had physical implications on films colors, reflecting different wavelengths of light (Figure 3b).

Figure 3. (a) Yttrium oxide growth rate and (b) Yttrium oxide physical appearance.

Figure 4. XPS surface analysis for the elements: Fe, O, Y and Cr.
Figure 4 shows the coating deposition history during the first 21 min, contemplating the regions: Fe 2p, Cr 2p, Y 3d and O 1s. The uncoated sample is represented by “Steel” in the graphics.

About the main Fe 2p and Cr 2p binding energies, the Fe<sub>x</sub>Cr<sub>y</sub>O<sub>z</sub> spinel was found on the native P91 surface at environmental conditions. The Fe 2p 3/2 peaks were found at ~706 eV and 708.8 eV, corresponding to the oxidation states Fe<sup>0</sup> and Fe<sup>2+,3+</sup>, respectively. Likewise for Cr 2p 3/2 peaks, confirming the presence of Cr<sup>0</sup> at 573.3 eV and Cr<sup>3+</sup> at 576.1 eV. Regarding to Y 3d region, the Y<sub>2</sub>O<sub>3</sub> oxide was determined by the representative binding energy Y 3d 5/2 at ~157 eV, whose contribution was growing in intensity with the deposition time, until leaving behind the Fe/Cr spinel layer [16].

3.2. Coatings evaluation under oxidizing conditions

As has been contrasted by several authors [2,17-20], the duplex oxide structure formed on the P91 steel corresponds to an outer layer rich in iron oxides and an inner one composed of Fe, Cr, Mn, Mo and Si oxides (Figure 5).

![Figure 5](image)

**Figure 5.** Duplex layer structure formed on 12-h coated P91 steel in steam, after 100 h at 650 °C.

The constituted morphology of the oxide layer showed that yttrium oxide was not effective in preventing the migration of Fe cations towards the gas interface, thus, hematite and magnetite phases were found at the bulk duplex layer (Figure 6).

![Figure 6](image)

**Figure 6.** Crystalline phases found at the oxide layer bulk on 12-h coated P91 steel, after 100 h in steam at 650 °C.

Farther, the perovskite YFeO<sub>3</sub> was probably identified close to the inner layer (Figure 6), which means that yttrium-oxide films tend to break down into these compounds, causing a slight reduction in the P91 corrosion rate.
Likewise, to determine the true protective coatings effect, the parabolic trending in Figure 7 indicated that the layer growth is dominated by elemental diffusion processes, inasmuch, the inner layer grows in the spaces left by the constant flow of cations towards the gaseous interface, continuously forming the typical duplex structure. Taking the previous arguments as reference, the inner layer was formed inside the alloy, which is equivalent to say that the length of material consumed is represented by its thickness. Consequently, the corrosion rates shown in Figure 8 were obtained, which were qualitatively severe according to the NACE RP0775-2005 standard (> 0.25 mm/y) [15]. Nonetheless, the different coatings managed to reduce the P91 deterioration rate in simulated oxidizing environment from the Colombian refinery. Notwithstanding, the thickness of the coatings did not show any particular effect, due to the accelerated diffusion processes that were promoted by the P91 severe oxidation in water vapor.

Figure 7. Mass gain for uncoated and coated P91 samples.

4. Conclusions
In this work, yttrium-based coatings were proposed to reduce the P91 corrosion rate in industrial oxidant environment. These coatings were deposited by PLD technique, giving rise to adherent and continuous films, whose growths were proportional to the laser abrasion time. In addition, prior to the oxidation studies, it was found that P91 steel develops a Fe/Cr spinel layer at normal conditions.
The coatings evaluation inside the carefully selected oxidation atmosphere at 650 °C gave place to oxide layers of duplex structure and limited protective behaviour. Although, through the formation of perovskites, it was possible to decrease the flow of cations through the oxide layers, causing a reduction in the corrosion rate of the P91 steel.

Finally, it is concluded that based REO coatings, such as yttrium oxide, have the potential to reduce the ferritic steels degradation rate. Nevertheless, the fail to prevent the P91 severe corrosion in industrial combustion conditions, by taking as a reference the evaluation window given by the first 100 h. Thus, other types of coatings should be evaluated to counteract the rapid Fe diffusion towards the external growth of fragile iron layers.

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