Characterization of films formed by the aluminizing of T91 steel

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Abstract. The aluminizing of a T91 martensitic ferritic steel was carried out by a novel modification to the traditional technique of packed cementation, with the objective of producing a diffusion coating of aluminum in a shorter time and operating cost, from a technique that allows the reuse of powder packaging and which the coating of metal parts with complex shapes can be secured. As an aluminum source, commercial foil is used to wrap the piece to be coated, while the powder packaging contains aluminum oxide Al₂O₃ and an activating salt, ammonium chloride NH₄Cl. During the deposition process of the coating, the NH₄Cl is decomposed by reacting with foil, and thus, aluminum halides can be transferred to the metallic substrate, which deposit aluminum on the T91 steel surface while Al₂O₃ can be recycled for subsequent processes. The results of the diffractograms and micrographs indicated the strong influence of temperature, exposure time and ammonium chloride concentration in the formation and growth evolution of a stable coating of iron-aluminum and iron-aluminum-nickel on the T91 steel surface, which was effectively deposited at a temperature of 700°C and an exposure period of 9 hours. The coating formed on the T91 steel surface could play a protective role towards the material by acting as a physical barrier between the alloy and other corrosive species in high temperature operated systems.

1. Introduction
The aluminizing of steels is widely used in industry because it can give low chromium alloys a protection against corrosion at high temperatures. One of the most used methods of aluminizing is the hot immersion of the parts to be covered in an aluminum bath. During this process, the piece is annealed in a pure hydrogen atmosphere at a temperature between 675 and 785°C. Subsequently, the piece is heated in a furnace with a non-oxidizing atmosphere to an approximated temperature of the aluminizing bath, with the objective of obtaining an aluminum coating with improved wettability and minimum uncoated points [1]. Finally, the hot piece is transferred to the aluminum and silicon bath, where the coating is obtained. Thus, is possible to realize the aluminizing of steel sheets that are commercialized by industries ranging from electrical appliances to the automotive industry, which manufacture multiple parts for high temperature applications such as ovens, mufflers, exhaust pipes, etc. The parts made from these aluminized sheets have zones that are sensitive to corrosion at high temperatures in the seams or adhesives of the sheets, as well as uncoated points, generating future damage to the material.

Another technique used for the aluminizing of steels that are subjected to high temperature corrosion conditions is the packed cementation, which is used in components for turbines, power generation plants, chemical applications, aerospace and petrochemical industries [2-3]. According to the process proposed...
by Bianco et al. [3-5], the process of aluminizing by packed cementation can be carried out at 900°C using sodium chloride and a powder alloy with 42% Al-58% Fe by weight, immersed in an argon atmosphere and a reforming gas (5% H₂+Ar). During heating in the furnace, the system is continuously rotated to eliminate the chemical depletion zone of the alloy powder within the package, wrapping the substrate with a ceramic sheet to produce a particle-free surface, and thereby, introducing a diffusion barrier for the transport of the gaseous species. This method has been used to obtain coatings by diffusion of aluminum, after 6 hours of reaction, of approximately 100 microns of thickness.

Other researchers proposed the use of CVD-FBR technique (Chemical vapor deposition by fluidized bed reactor) for aluminizing martensitic ferritic steels using 99.5% pure aluminum powder. The mixture was fluidized with analytical argon as an inert gas, hydrogen chloride with purity of 99.99% as the reactive gas, and analytical type gaseous hydrogen as reducing gas. With this process, Fe₂Al₅ coatings of 4μm thickness could be obtained at 550°C and 2 hours of material exposure time [5-7].

In the present study, a new aluminizing process was standardized, in which, commercial foil is used as an aluminum source and it wraps the piece to be covered, providing a concentrated source of aluminum throughout the process for growth and formation of the coating. This is in the closest area to the substrate surface, making the aluminum deposition process more efficient. The aluminizing by applying packed cementation in T91 steel, using commercial foil as a source, contributes in the industry because more efficient and economic processes are standardized, which are developed at low temperatures and short operating times in comparison with other techniques that are used nowadays.

2. Experimental

The coupons for the gravimetric tests are machined in rectangular form with dimensions of: 2×1×0.5cm from a martensitic ferritic steel (Fe-9Cr-1Mo), which are characterized based on ASTM E-415 standard [8] using an optical emission spectrometer. The surface of the coupons is prepared metallographically by using silicon carbide sandpaper, treatment initiated with sandpaper No. 120 up to No. 2400, based on ASTM G31-72 standard [9]. Prior to the tests, the coupons were cleaned with ethanol and then with acetone in an ultrasonic bath.

For all the tests, a horizontal tubular type batch furnace is used. Powder pack mixtures are prepared with a composition of 94% Al₂O₃ and 6% NH₄Cl by weight, which are carried to a ball mill for 24 hours to obtain a homogenization of the mixture. The gravimetric coupons are wrapped in commercial foil pre-treated by oxidation at 500°C, and then soaked in the powder package into alumina crucibles. The crucibles are introduced into the horizontal tubular furnace and exposed to a continuous flow of high purity analytical nitrogen. This procedure is carried out at temperatures of 500, 600 and 700°C, and operating times of 3, 5 and 9 hours.

3. Results and discussion

The oxidation pre-treatment at 500°C of the commercial foil is carried out in order to promote the growth of an aluminum oxide thin layer on its surface, and thereby, avoid that the aluminum of the foil melts on the metallic substrate at temperatures above the aluminum melting temperature, equivalent to 660°C, which would produce an irregular and non-homogeneous surface. The result of pre-treatment is presented in Figure 1 where it is possible to observe, in addition to the large pores, the formation of a fine porosity along the foil entire surface. This commercial foil pre-treatment process leads to the formation of a number of fine pores, which increases with the oxidation time and provides the diffusion paths for the volatile species generated by the breakdown of the salt, which subsequently react with the aluminum inside the foil to produce the volatile aluminum halides that effectively deposit the aluminum for forming the coating. Therefore, the smooth surface of the coated coupons shows that the coating was formed by gaseous species and not by aluminum which melted and deposited during the coating process, since on this last case, metallic deposits would be observed completely adhered to the surface of the steel substrate as reported in other cases where aluminum powder was used [3].

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Figure 1. Characteristic porosity of commercial foil after pre-treatment.

The thickness of the coatings obtained by the aluminizing of the martensitic ferritic T91 steel coupons exposed to system temperature conditions of 500, 600 and 700°C, times of 3, 5 and 9 hours, and pressure of 5psi in N₂ atmosphere are detailed in Figure 2. It is observed that at longer exposure times, the thickness of the coating formed by the diffusion of aluminum on the T91 steel surface has an increasing behavior, where the process is carried out with an optimum concentration of 6% by weight of NH₄Cl in the system. On the contrary, it was not possible to aluminize T91 steel by this technique at a temperature of 500°C, regardless of the operating time.

Figure 2. Variation of the coating thickness at different operating conditions.

In the micrographs of Figure 3, the thickness of the coatings obtained on the T91 steel surface is evident at system temperatures of 600 and 700°C, and exposure times of 3, 5 and 9 hours. A smooth light gray surface is detailed in the micrographs in all the coatings formed under the above conditions. Moreover, it was evident that the obtained coatings are continuous, of homogeneous thickness, thermodynamically stable, with pore-free morphology and without evidence of unstuck parts, obtaining an increase in the coating thickness formed on the T91 steel surface in a range from 53 to 205μm.
X-ray diffraction was performed on the exposed coupon at 700°C for 9 hours, which shows that the crystalline phases present with greater intensity correspond to compounds of FeAl and Fe_{0.99}Al_{0.99}Ni_{0.02} on the aluminized T91 steel surface, which are listed in Table 1. Likewise, in the micrograph of Figure 4 is observed that the aluminum coating on the T91 steel surface consists of two layers, which are identified from the diffractograms as Fe-Al (layer 1) and Fe-Al-Ni (layer 2).

**Table 1.** Phases found in the coating formed on the steel surface exposed to 700°C, 9 hours and NH_{4}Cl 6%w/w.

| Crystalline phases | Name                      |
|--------------------|---------------------------|
| Fe_{3}O_{4}        | Magnetite                 |
| Fe_{2}O_{3}        | Hematite                  |
| FeCr               | Iron-Chrome               |
| FeAl               | Iron-Aluminum             |
| Fe_{0.99}Al_{0.99}Ni_{0.02} | Iron-Aluminum-Nickel          |
4. Conclusions
It is possible to generate a coating on a martensitic ferritic steel by diffusion aluminizing from commercial foil at temperatures of 600 and 700°C, and exposure times from 3 to 9 hours. The oxidation pre-treatment applied to the commercial foil is enough to prevent the aluminum from melting on the steel surface during the coating process. The technique can be applied at temperatures above the melting temperature of aluminum, which allows to obtain coatings in shorter times compared to the traditional ones. By the application of the X-Ray Diffraction technique, the main compounds present in the coating were identified as FeAl and Fe$_{0.99}$Al$_{0.99}$Ni$_{0.02}$. The use of commercial foil instead of aluminum powder as a source makes the T91 steel aluminizing process efficient and cost-effective because it considerably reduces the costs of raw material, in addition to reducing energy consumption by performing the process in a shorter time than traditionally required to achieve coating of more than 100 microns in thickness.

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