BEHAVIOR OF ALUMINUM COATING BY CVD-FBR IN STEAM OXIDATION AT 700°C

COMPORTAMIENTO DEL RECUBRIMIENTO DE ALUMINIO POR CVD-FBR EN LA OXIDACIÓN EN VAPOR A 700ºC

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ABSTRACT

Aluminum coatings have been obtained using the Chemical Vapor Deposition of Fluidized Bed Reactor technique (CVD-FBR), on austenitic stainless steels (AISI 304, AISI 316 and AISI 317), in order to evaluate resistance to steam oxidation at 700°C. The coatings were characterized in their morphology/ composition and crystalline phases using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX) and X-ray Diffraction (XRD). In addition, thermodynamic simulation was performed using Thermo-Calc® software to make the deposition of the coating on said steels similar to optimal conditions. All specimens -with and without aluminum coating by CVD-FBR- were oxidized at 700°C, in a steam atmosphere of nearly 100% for 1000 h. The aluminum coating prevented the formation of oxide islands or crust, and reduced steel mass gain. Coated AISI steel showed a 25% reduction in mass gain compared to the same steel uncoated and oxidized under the same conditions. AISI 316 and AISI 317 steels underwent loss of mass because the brittle oxide that was formed came loose.

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RESUMEN

S e han obtenido recubrimientos de aluminio por la técnica de deposición química de vapor por lecho fluidizado (CVD-FBR de sus siglas en inglés), sobre aceros inoxidables austeníticos (AISI 304, AISI 316 y AISI 317), con el propósito de evaluar la resistencia a la oxidación en vapor de agua a 700°C. Los recubrimientos fueron caracterizados en su morfología/composición y fases cristalinas mediante las técnicas de Microscopía Electrónica de Barrido (MEB), con análisis de rayos X por dispersión de energía (EDAX de sus siglas en ingles) y Difracción de Rayos X (DRX). Además, se realizó simulación termodinámica mediante el software comercial Thermo-Calc®, con la finalidad de aproximar a las condiciones óptimas la deposición del recubrimiento sobre los mencionados aceros. Todos los especímenes sin y con recubrimiento de aluminio por CVD-FBR, fueron oxidados a la temperatura de 700°C, en una atmósfera próxima al 100% de vapor de agua por 1000 h. El recubrimiento de aluminio evitó la formación de islas o costra de óxidos y disminuyó la ganancia de masa de los aceros. El acero AISI 304 con recubrimiento presentó una reducción del 25% en la ganancia de masa en comparación con el mismo acero sin recubrimiento y oxidado en las mismas condiciones; los aceros AISI 316 y AISI 317 presentaron pérdida de masa, debido a que el óxido formado se desprende por su naturaleza quebradiza.

Palabras clave: *Recubrimientos de aluminio, Deposición química por lecho fluidizado (CVD-FBR), Corrosión a alta temperatura, Oxidación en vapor de agua, Aceros inoxidables austeníticos.*

RESUMO

F oram obtidos recobrimentos de alumínio pela técnica de deposição química de vapor por leito fluidizado (CVD-FBR por suas siglas em inglês), sobre aços inoxidáveis austeníticos (AISI 304, AISI 316 e AISI 317), com o propósito de avaliar a resistência à oxidação em vapor d'água a 700°C. Os recobrimentos foram caracterizados em sua morfologia/composição e fases cristalinas mediante as técnicas de Microscopia Eletrônica de Varredura (MEB), com análise de raios X por dispersão de energia (EDAX por suas siglas em inglês) e Difração de Raios X (DRX). Além disso, foi realizada simulação termodinâmica mediante o software comercial Thermo-Calc®, com a finalidade de aproximar às condições ótimas a deposição do recobrimento sobre os mencionados aços. Todos os espécimes, sem e com recobrimento de alumínio por CVD-FBR, foram oxidados à temperatura de 700°C, em uma atmosfera próxima a 100% de vapor d'água por 1000 h. O recobrimento de alumínio evitou a formação de ilhas ou camada de óxidos e diminuiu o ganho de massa dos aços. O aço AISI 304 com recobrimento apresentou uma redução de 25% no ganho de massa em comparação com o mesmo aço sem recobrimento e oxidado nas mesmas condições; os aços AISI 316 e AISI 317 apresentaram perda de massa, devido a que o óxido formado se solta por sua natureza quebradiça.

Palavras-chave: *Recobrimentos de alumínio, Deposição química por letio fluidizado (CVD-FBR), Corrosão a alta temperatura, Oxidação em vapor d'água, Aços inoxidáveis austeníticos.*

1. INTRODUCTION

Chemical Vapor Deposition by Fluidized Bed Reactor (CVD-FBR) is a process that combines the main advantages of fluidized beds, which are: temperature uniformity, mass and heat transfer, and a high degree of gas mixing with fluidized particles. The aforementioned lead to the reaction of all the active species in the bed, combined with the benefits of chemical vapor deposition, such as the ability to control with relative ease the composition of the deposited material, obtaining single, multiple or compound layers, and in general, structured nano materials with dimensions smaller than 1 µm (Lau, Sanjurjo & Wood, 1992; Anthymidis, Stergioudis & Tsipas, 2001). The CVD-FBR process enables the deposition of coatings in the temperature range from 300 to 900ºC, obtaining a variety of wear resistant layers of *C, N, CN, Ti, V, Cr, Nb, Ta, Mn, W* and *Mo* on several types of metals such as *Fe, Ni, Co* and the alloys thereof (Pierson, 1999; Arai, Takeda & Endo, 1989). In addition, by means of CVD-FBR at one atmosphere of pressure, coatings have been obtained in a temperature range from 300 to 1200ºC, of *Al, Cr, Si, B* and *Ti*, in order to improve the behavior of ferritic and austenitic steels against oxidation, corrosion at high temperatures and wear (Stoloff, Liu & Deevi, 2000; Lau *et al.*, 1992; Bolívar, 2007).

In recent years, research has been done on obtaining coatings that will make it possible to reduce oxidation problems and contribute to increasing operating temperatures of thermal power plants, without the materials losing their mechanical, structural and morphological properties. That is why studies have been conducted on *Al, Mn, Si, Ti-N, Cr-N, Al-Mn, Al-Si* and other coatings applied by CVD, deposited on different steels (ferritic, martensitic, austenitic, etc.) These coatings reached a thickness of 10 µm on average and were evaluated in extreme steam oxidation conditions at temperatures from 500 to 800ºC (Maitra & Gupta, 2003; Ehlers *et al.*, 2006; Agüero *et al.*, 2007; Bolívar, 2007). The increase in operating temperature would improve the thermal efficiency of power generation plants, thus reducing the quantity of fossil fuel used and the emissions of greenhouse gases such as CO_2, SO_2 and NO_x. These are known for being harmful to the atmosphere, the climate and the future of the planet

(Ennis & Czyrska-Filemonowicz, 2003). The aluminum coating deposited by CVD has oxygen affinity, thus allowing the formation of the layer of alumina (Al_2O_3), which increases protection against steam oxidation (Sánchez, Bolívar, Hierro & Pérez, 2009; Marulanda, Castañeda & Remolina, 2013; Bolívar, 2007).

Lau *et al*. (1992), studied the reactions of the *Al* bed and activator gases $HCl(g)+H_2$ in the temperature range from 127 to 627°C, using a mass spectrometer to obtain information on the growth process of the *Al* coating on *Cu* by CVD-FBR. Based on the results, it was verified that the halogenated precursors formed were aluminum chlorides $Al_3Cl(g)$ and $AlCl(g)$. It was observed that $AlCl(g)$ was the most important gas precursor in the mechanism to form the layer of *Al*. The authors managed to deposit a fine layer of *Al* on copper wire using a mixture of *Ar* with 0.12% *HCl* and 7% of H_2 by volume.

Pérez *et al.* (2001) researched the obtainment of the *Al* coating at temperatures below 600°C by CVD-FBR (Sánchez *et al.*, 2009). In order to do so, they used a bed formed by *Al* dust, which was fluidized with *Ar* using the mixture of HCl/H_2 gases as an activator. The experiments were conducted in the temperature range from 500 to 600°C on different types of substrates, such as ferritic stainless steels, austenitic stainless steels and *Ni*-based super alloys. By using this system, they managed to obtain homogeneous coatings formed by the intermetallic compounds Fe_2Al_5 and $FeAl_3$, for the *Fe* alloys. For the *Ni* alloys, it was determined that the layers were formed mainly by Ni_2Al_3 and *NiAl*.

This paper evaluates the advantages of the aluminum coating deposited using the CVD-FBR technique on austenitic stainless steels, in order to improve resistance to steam oxidation of the substrate. The coatings were treated thermally to form layers or iron aluminides (intermetallic compounds) on the respective steel, responsible for protection against steam oxidation, because they act as a source of aluminum for the formation of alumina (Al_2O_3), upon contact with steam during oxidation. Due to the high melting point of alumina, this protective layer prevents the volatilization of chromium during steel oxidation, in the form of oxides, hydroxides and chromium oxyhydroxides, which are volatile species that have been reported in

other papers (Ebbinghaus, 1993; Asteman, Svensson & Johansson, 2002; Pérez & Castañeda, 2007). In austenitic steel without aluminum coating, oxidation accelerates at 700ºC due to the presence of steam, forming major crusts or islands of iron oxides, among which wustite (*FeO*) is the most harmful. There is also a considerable increase in the thickness of the oxide in the order of millimeters, creating internal strain with the substrate due to the size. This results in the oxide breaking and detaching from the substrate, which is in line with Asteman *et al.* (2002).

2. EXPERIMENTAL PROCEDURE

Preparation of Substrates

The tubes of uncoated austenitic stainless steel (AISI 304, AISI 316 and AISI 317) were machined in dimensions of 20 mm long x 6 mm wide x 2 mm thick, sanded using *SiC* emery paper from No. 100 to No. 600, and finally cleaned in an acetone bath by ultrasound for 10 minutes. The dimensions of all the test tubes were measured using a Vernier gauge with an accuracy of 0.05 mm.

Thermodynamic Simulation

Thermodynamic simulations were conducted using the Thermo-Calc program (Thermo-Calc®, 2003) to estimate the deposition parameters of the *Al* coating by CVD-FBR. Theoretic calculations are an initial approximation of the coating deposition conditions on the metal substrates, taking into account substrate temperature, pressure (1 atm), percentages of reactant gases (H_2 and *HCl*), inert fluidizing gas (*Ar*), aluminum as filler material and fluidized bed material (Al_2O_3), among others. The estimated parameters were tested using experimental deposition, and those that demonstrated the best behavior were selected. Thermodynamic simulation consisted of analyzing the precursors that could be formed upon passage of the *Ar, HCl* and H_2 gases. In addition, to achieve better aluminum coating, bed mass was estimated based on the proportions of the gases mentioned above. The simulation was carried out in the 500 to 660ºC temperature range, which was chosen based

on previous papers (Pérez *et al.*, 2001), in order to refine and improve coating deposition parameters. Furthermore, thermodynamic simulations of vapor oxidation were conducted on steel with and without *Al* coating, and in conditions similar to pilot tests. This was done to estimate the possible solid phases of oxides and gaseous species that could be formed during the respective testing. Thermo-Calc®, is a thermodynamic simulation program based on the Gibbs free energy minimization method, which calculates the thermodynamic balance of each simulated process.

Coating Deposition

The aluminum coatings were deposited by CVD-FBR at atmospheric pressure. The beds used were composed of aluminum dust of a purity by weight of 99.55%, with an average particle size of 400 μm, being alumina (Al_2O_3) used as a fluidized bed. The dust mixture was fluidized by inert argon gas (*Ar*) of a purity by weight of 99.999%. In addition, hydrochloric acid (*HCl*) –of a purity by weight of 99.999%– was used as a reactive gas, and hydrogen (H_2) –of a purity by weight of 99.999%– was used as a reductive gas. The coatings deposited were heat-treated in the same reactor, in an argon atmosphere at 700ºC for 4 hours, in order to form the desired iron aluminides on the surface. All the substrates –with and without coating– were weighed on an analytical balance with an accuracy of 10^{-5}g.

Steam Oxidation

Samples were oxidized in a steam atmosphere at 700ºC in a closed, cyclic oxidation reactor "Oxidation *Loop*" (Commercial instrument of Iberlabo S. A., Madrid, Spain). The system is made up of a steam generator with two furnaces at a constant temperature, one to generate steam and the other where the test samples are placed: type K thermocouples (chromel/alumel), gas controllers, pressure gauges, a water pump, teflon hoses, a quartz container to store water and steam condensers, among others (Marulanda, 2013). The steam is transported to the loop by a continuous flow of 2.4 ml/min of water and an N_2 gas flow of 1700 ml/min. All the samples in this paper were oxidized in an atmosphere of approximately 100% steam during 1000 h of exposure. 16 samples were presented in each oxidation test, all of which were of the same material (austenitic stainless steel with or

without coating). In order to observe the respective oxidation kinetics (mass vs. time gradient) of each sample, two samples were removed systematically at oxidation time intervals of 24, 50, 100, 200, 400, 600, 800 and 1000 h. They were all previously cooled in dry air to be weighed on the analytical balance. The morphology of the oxidized samples was characterized by Scanned Electron Microscopy (SEM). The crystalline phases present in the coatings were identified by X-ray Diffraction (XRD), in modes of (θ-2θ) and grazing angle, composition by Energy Dispersive X-ray Analysis (EDAX), and, in the surface, concentration profile and volume analysis.

30 µm

Figure 1. Surface image acquired by SEM of the AISI 316 austenitic stainless steel coated with aluminum by chemical vapor deposition on a fluidized bed.

3. RESULTS AND ANALYSIS

Simulation results indicated that aluminum halides such as $AlCl_3$, $AlCl_2H$, $AlCl$, Al_2Cl_6 could be generated, along with others in smaller proportions, such as: $AlCl_2$ and $AlClH_2$. In order to verify the theoretic results of thermodynamic simulation, experimental Al deposition tests were conducted systematically on austenitic AISI 304, AISI 316 and AISI 317 steels by CVD-FBR, until the best Al coating was found. That is to say, the thickest one with the most compact surface, best crystallinity and best thickness uniformity, among others. Results indicated that the best conditions occurred when the coating was deposited at a temperature of approximately 580ºC for 1.5 h, in a bed consisting of 10% by weight of aluminum dust and 90% by weight of inert bed (alumina), with a 1/18.5 HCl/H_2 activator gas ratio. The active and neutral gas rate is 38% by volume of active gases and 62% by volume of neutral Ar gas.

Figure 1 illustrates the image acquired by SEM at 1800 x of the surface of a sample of Al coating deposited on AISI 316 steel. It shows a surface with a rough morphology and the growth of globular grains of circular nucleation, and the formation of apparent cones with a porous constitution in the form of flakes. The chemical composition analysis by EDAX of the sample surface indicated a content in percentage by weight of: 50% of Al, 26% of Fe, 10% of Cr, 11% of Ni, 1% of Mn and a minor diffusion of Mo of the substrate of 0.88%.
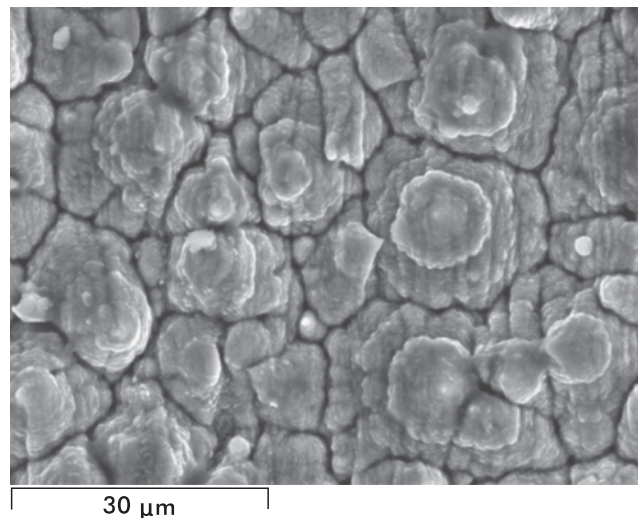
The coating of Al by CVD-FBR on coated austenitic steels proved to be homogeneous, compact, crystalline and had a minimal variation in thickness of 8% (+/- 2.5 µm). Figure 2 illustrates two cross sections with the respective line analysis there of, showing the concentration profile of the aluminum coating on the AISI 304 stainless steel substrate, with and without thermal treatment in Ar at 700ºC. Results showed an atomic 75% Al on the surface of the sample without treatment (Figure 2a), which decreases to nearly atomic 40% Al in composition near the substrate-coating interface. They also showed Fe concentrations between atomic 20 and 30%, Cr between atomic 10 and 20%, and a minor amount of Ni up to atomic 10% dissolved in the coating. The largest Ni concentration on the surface corresponds to the metallization of the sample to prevent the coating from breaking when subjected to grinding or polishing for observations by SEM. The line analysis by EDAX in Figure 2b shows the chemical concentration profile of the sample with thermal treatment, clearly showing the diffusion of Al near the inside of the steel and Fe near the surface, which according to the stoichiometry thereof may be approximated to certain iron aluminides such as $FeAl$.

XRD analysis of the samples determined the presence of phases of: $Al_{13}Fe_4$, Fe_2Al_5, $FeAl_2$ and Al_5FeNi in the sample without thermal treatment. The sample with
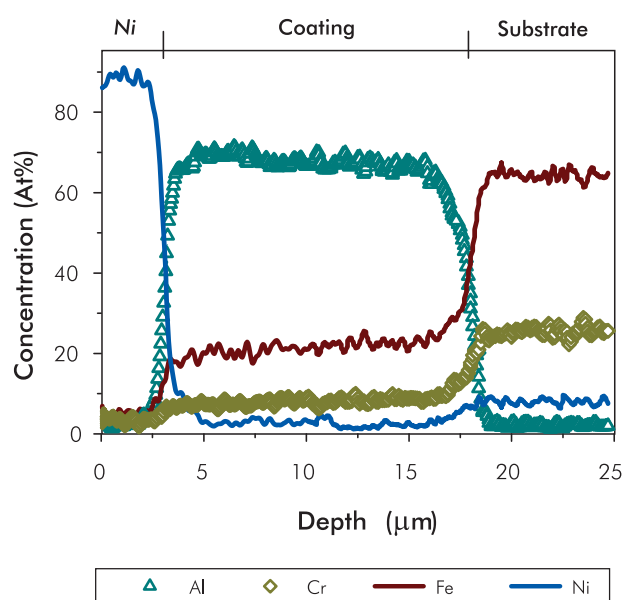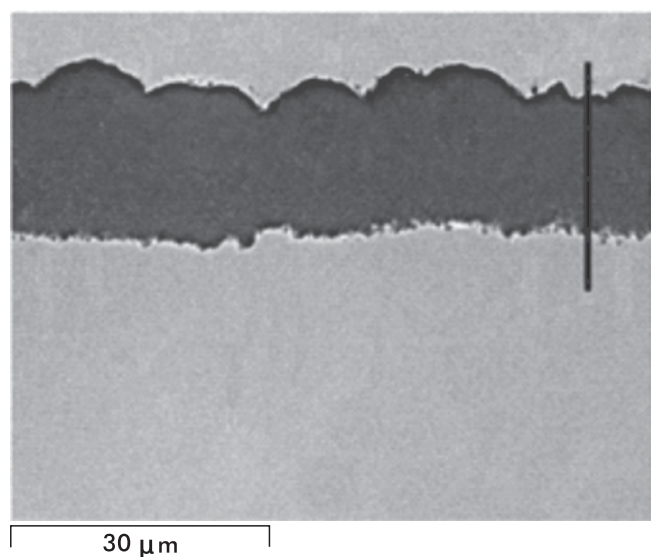
(a)
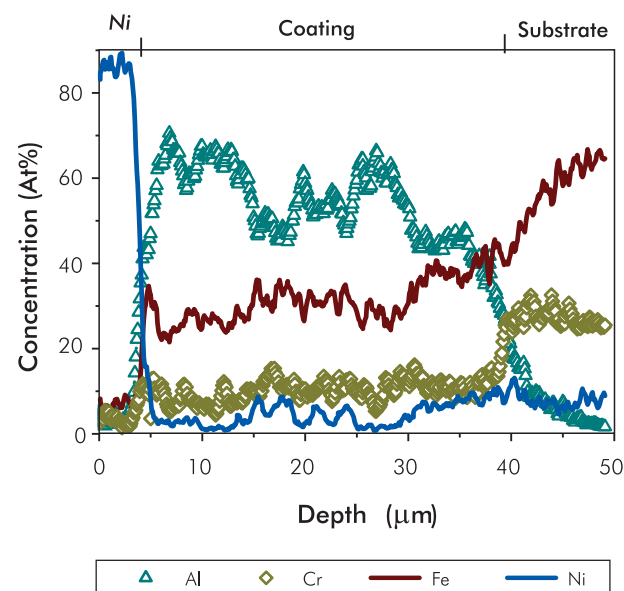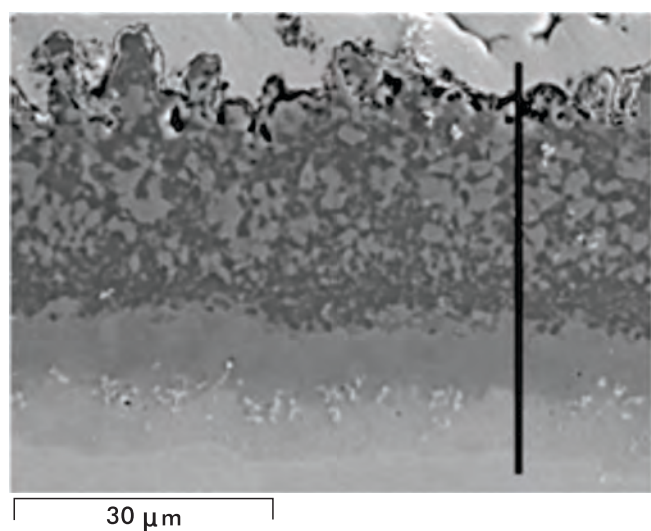
(b)

Figure 2. Concentration profile of AISI 304 stainless steel coated with *Al* by CVD-FBR; (a) Sample as deposited without thermal treatment. (b) Sample with thermal treatment at 700°C in *Ar* for 4 h.

treatment showed the phases of *FeAl*, $Al_{0.99}Fe_{0.99}Ni_{0.02}$, *AlNi* and *Fe₂AlCr*. The results confirmed the composition analysis by EDAX illustrated in Figure 2, which validates the effect of thermal treatment in relation to the crystallinity of the sample, indicating the presence of the *FeAl* phase, considered stable and acting as a source

of *Al* for the formation of the alumina layer, and helping to protect the sample from steam oxidation at 700°C.

The results of thermogravimetry of the samples are illustrated in Figure 3. According to uncoated oxidized steels (Figure 3a), it can be confirmed that AISI 304

steel showed the least mass gain because it was best protected by the formation of a layer of chromium rich oxide. Furthermore, AISI 316 steel lost the most mass, forming a layer of iron-rich oxide, and AISI 317 steel lost the least amount of mass forming a layer with iron and chromium oxides. It is important to point out that the oxides formed on the latter two uncoated steels proved to be very fragile, to the extent that at the end of each test -when the oxide husk became thicker than 50 μm-, and when they were cooled and weighed, they broke easily. Therefore, the mass variation curves of the oxidized samples of AISI 316 and AISI 317 steels, without *Al* coating, underwent an apparent mass loss, not considering the amount of oxide that was fractured or detached from the sample. The oxidized sample of AISI 304 steel retained its oxide, and its mass variation curve was used as reference for comparison with the mass variation curves of steels with aluminum coating.

The thermogravimetry of the steels with *Al* coating is shown in Figure 3b. It is found that *Al* coating plays an important role, as it helps to decrease the oxidation rate of the steel and increases protection in these aggressive conditions of steam oxidation. For instance, the *Al* coating deposited on AISI 304 steel underwent a reduction of nearly 25% in mass gain during oxidation,

compared to the same oxidized substrate in equal conditions, Figure 3b.

The results show that the aluminum in the coating and the iron of the substrate form iron aluminide or intermetallic phases, which wind up becoming the base material for the formation of the protective layer of Al_2O_3 during oxidation. This layer has a high thermal expansion coefficient and major chemical stability, thus preventing or delaying the steel's loss of chromium by volatilization. In this phenomenon, the gaseous species appear in the form of oxyhydroxides, hydroxides or chromium oxides, $CrO_2(OH)_2(g)$, $CrO_2(OH)(g)$, $Cr(OH)(g)$, $Cr_2O(g)$, $Cr_2O_3(g)$, formed by contact with steam. These species were not studied herein, but they have been reported in other papers (Ebbinghaus, 1993; Castañeda, Bolívar & Pérez, 2010). The layer of alumina (Al_2O_3) and the chromium oxide (Cr_2O_3) are responsible for the protection of steel against oxidation in steam. When the uncoated steels are oxidized, they lose the critical percentage of chromium by reaction and/or volatilization, thus decreasing the protection against oxidation and accelerating the oxidation rate, causing a larger amount of iron oxides (hematite, wustite and magnetite) to form on the surface, which is why these steels undergo mass gain.
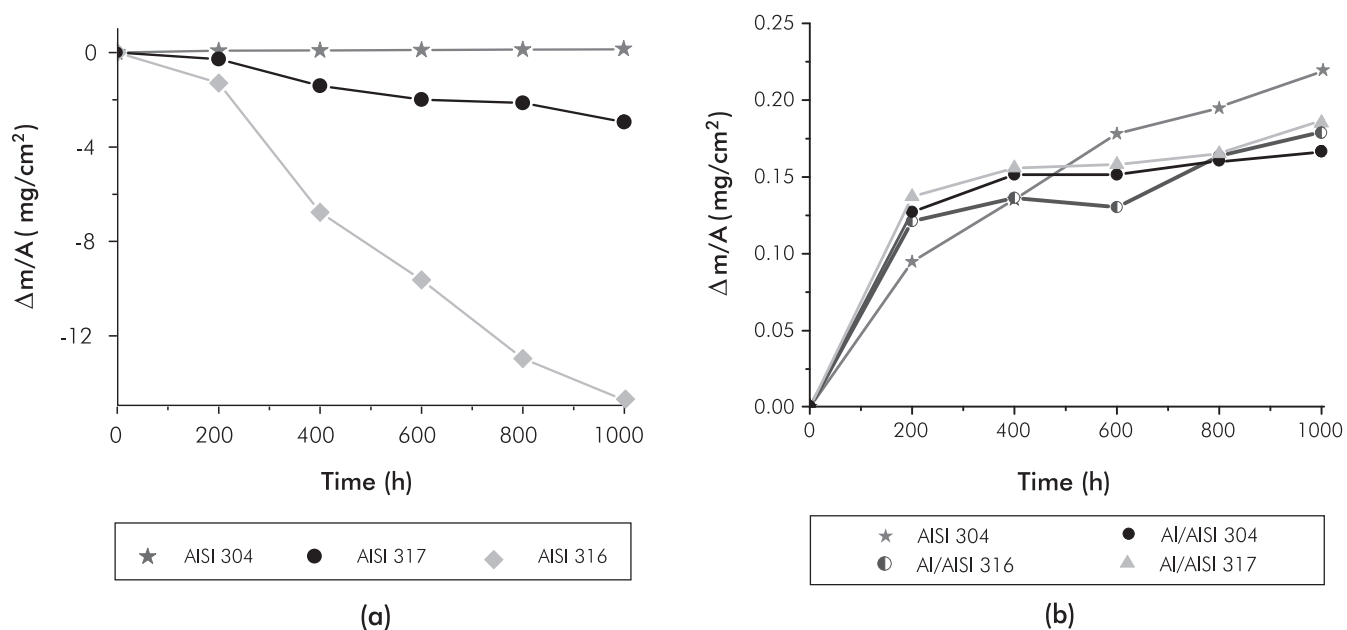

(a)

(b)

Figure 3. Variation in mass vs. Oxidation Time at 700°C of AISI 304, AISI 316 and AISI 317 steel (a) Oxidation of the three austenitic steels without *Al* coating (b) Oxidation of the three steels with *Al* coating and compared to the oxidized AISI 304 substrate.

Of the three austenitic steels, AISI 304 steel was the one with the best behavior toward steam oxidation because it had a higher concentration of *Cr, Mn* and *Si*. During oxidation, this steel may form other protective oxides such as silica *(SiO₂)*, and/or mixed spinels or mixed *Cr, Si* and *Mn* oxides. AISI 316 steel formed the most oxides and had the lowest protection against steam oxidation, because it formed an outer layer of iron-rich oxides, which are porous. On the other hand, the AISI 317 steel showed an intermediate behavior, forming a layer with a mixture of chromium oxides and iron oxides. The loss of mass observed in AISI 316 steel, Figure 3a, is possibly related to the low adherence of the oxides formed or due to the microstrain caused by thermal changes when extracted from the oxidation loop, which break and detach from the sample evaluated, showing less protection.

Figure 4 shows a SEM micrograph by detection of backscattered electrons from the cross section of the AISI 316 steel, oxidized by steam at 700ºC during 4 h of exposure. The image shows the presence of oxide husks from two areas: one outer area formed by a porous layer that is 30 μm thick (gray area with light areas), rich in iron and oxygen detected by EDAX analysis, with possible iron oxides: wustite *(FeO)*, hematite *(Fe₂O₃)* and magnetite *(Fe₃O₄)*. This area has a fragile appearance and/or low adherence, considering that it detaches when the sample is weighed. Its internal transport of oxygen from the dissociated gas is facilitated and, together with the disseminated iron from the steel, form the respective oxides based on their valence. Inside the oxide husk, there is another area (light gray area) formed by a compact, uniform layer of approximately 25 μm thick. This area is rich in *Cr, Fe* and *O*, where the chromium oxide is formed, along with protective mixed oxides and spinels that were identified by XRD.

The degradation and loss of protection to the oxidation of the steel is the result of the critical loss of chromium by volatilization, possibly due to the interaction between chromium oxide *(Cr₂O₃)* and steam, forming volatile species of chromium, such as: *Cr₂O(OH)₂(g)* or *CrO₂(OH)(g)* (Ehlers *et al.*, 2006; Cheng, Kuan & Tsai, 2006; Nasution, Velasco & Kim, 2009).
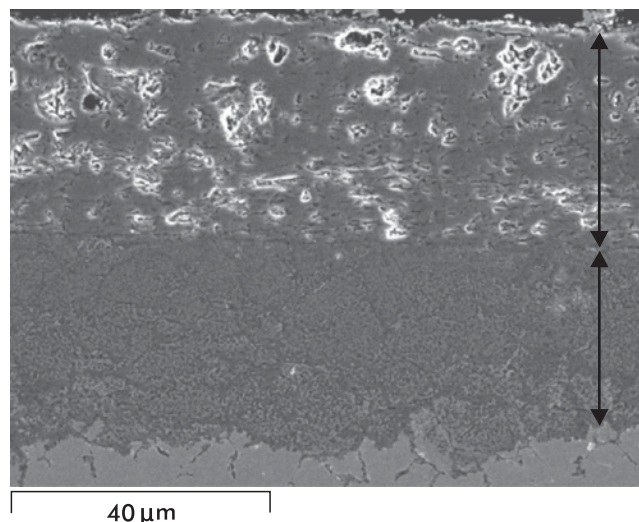

Figure 4. Cross section of the AISI 316 stainless steel substrate, oxidized in steam at 700°C for 400 h.

Figure 5 shows Micrograph by SEM at 1200 x, using backscattered electron detection of the cross section of the AISI 316 steel sample and coated with *Al* oxidized at 700ºC for 1000 h. There is a coating thickness of approximately 45 μm. In this figure, three areas are apparently observed; first of all, an outer porous layer (light gray area), which -according to EDAX composition analysis- is made up on the surface of atomic 70% aluminum and approximate atomic 15% oxygen, where the *Al₂O₃* is possibly formed. The aluminum and oxygen diffuse toward the substrate, finding an atomic 10% of aluminum and an atomic 3% of oxygen at 50 μm of the substrate. This diffusion causes the empty spaces -or pores- observed during oxidation. In addition, a nickel content of approximately atomic 10% is observed, along with iron between atomic 30 and 70% and chromium between atomic 20 and 30%, which diffuse from the substrate.

In the intermediate area, which corresponds to a mixture of light and dark gray, small qualities of *Al, Ni, Fe, Cr* and *Mo* are observed. XRD analyses confirm that the outer layer is *Al₂O₃* and the other layers correspond to phases of iron aluminides, such as *FeAl*, *Fe₃Al*, *Fe₀.₅₂Cr₁.₃₆*, *AlFe₀.₂₃Ni₀.₇₇*, and intermediate phases of *AlNi* and *(Al₁₋ₓCrₓ)₂O₃*. The last area, according to the composition, is the AISI 316 steel substrate. In conformity to these results, it can be verified that the aluminum coating protects the steel from oxidation in

steam at 700ºC, since the coating forms a protective layer of alumina (Al_2O_3) upon contact with the steam. In addition, intermetallic or iron aluminides are formed, which work as a thermal barrier of these critical conditions of oxidation.
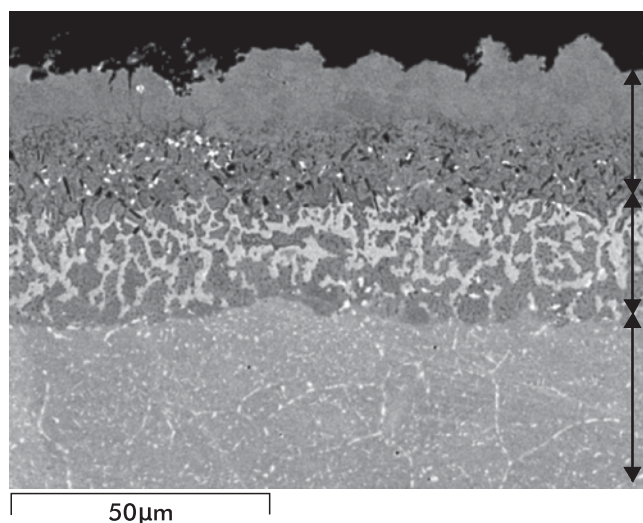

Figure 5. Cross section of AISI 316 stainless steel coated with aluminum by CVD-FBR and oxidized in steam at 700°C for 1000 h.

4. CONCLUSIONS

● The aluminum coating contributes to resistance to steam oxidation of AISI 304, 316 and 317 austenitic stainless steels, due to the formation of iron aluminides (intermetallic), which provide a source of aluminum during oxidation. This results in the formation of a protective layer of alumina (Al_2O_3), which is compact, adherent and, due to its high melting point, prevents loss of Cr by volatilization. In addition, it favors the formation of protective phases, such as nickel and chromium-rich spinels, underneath the coating.

● The Al coating applied by CVD-FBR achieved a reduction of approximately 25% in mass gain in AISI 304 steel, compared to the results obtained in the same steel without coating, oxidized in steam at 700ºC.

● The aluminum coating deposited by CVD-FBR on the AISI 304, 316 and 317 austenitic stainless steels protects and/or delays the oxidation rate in supercritical steam conditions at a temperature of 700ºC, to the extent that the application of this coating could increase the operating temperature of the thermal plants, thus increasing efficiency and decreasing gas emissions.

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