Materials Science Forum *Online: 2008-09-09*
ISSN: 1662-9752, Vols. 595-598, pp 359-366
doi:10.4028/www.scientific.net/MSF.595-598.359

Evaluation of Al-Hf Coating on Ferritic Steels by CVD-FBR Technology in Steam Oxidation

F. J. Bolívar[1,3], L. Sánchez[1], M. P. Hierro[1], J. A. Trilleros[1,2], F. J. Pérez[1]

[1]Grupo de Investigación de Ingeniería de Superficies y Materiales Nanoestructurados

[2]Grupo de Investigación en Ingeniería Metalúrgica - Facultad de Ciencias Químicas Universidad Complutense de Madrid.

[3]Grupo de Corrosión y Protección Universidad de Antioquia

28040 Madrid Spain

fjperez@quim.ucm.es

Keywords: A. Iron aluminides, based on FeAl; C. Coatings, intermetallic, Steam oxidation; C. Vapor deposition

Abstract. The steels with chromium contents between 9 and 12%wt are used for power plants with advanced steam conditions. These steels possess good creep properties similar to the 9% Cr steels as well as good creep and good oxidation resistance at temperatures between 500-600°C. In the last years efforts have been made to develop coatings for protection against oxidation in order to allow operation of steam turbines at 650°C. In this study, Al-Hf protective coatings were deposited by CVD-FBR on the ferritic steel HCM-12A followed by a diffusion heat treatment, and were shown to be protective at 650°C under steam for at least 3000 hours of laboratory steam exposure under atmospheric pressure. The morphology and composition of the coatings were characterized by techniques, including scanning electron microscopy (SEM), electron probe microanalysis, and X-ray diffraction (XRD). The results showed a substantial increase of steam oxidation protection afforded by Al-Hf coating deposited by the CVD-FBR process.

Introduction

The goal of improving the efficiency of power plant, by increasing the temperature and pressure of the steam, has been pursued for many decades. For example, using a 538°C /18.5 MPa steam plant as the base case, an efficiency increase of nearly 6% is achieved by increasing the steam conditions to 593°C/ 30 Mpa. At 650°C, the increase in efficiency is as much as 8%. An improvement in the thermal efficiency of the plant not only reduces the fuel costs but also reduces the release of SO_2, NO_x, and CO_2 emissions per unit of coal burned [1].

Ferritic and martensitic heat-resistant steels with Cr content between 9-12%, have been developed for uses such as main steam pipes and superheater tubes in power generation boilers [2, 3]. These steels were developed to have higher creep strength than the conventional ferritic steels. In particular, the use of 9-12% Cr steels up to 650°C is expected to be the key to increasing the power plant efficiency. However, the life-time of boiler materials is determined not only by their creep strength but also by their steam and fireside-corrosion resistance.

In this work, Al-Hf diffusion coatings by chemical vapor deposition in a fluidized bed reactor CVD-FBR were deposited on ferritic steel HCM-12A. The initial parameters of the processes were optimized by thermodynamic calculations using the Thermo-Calc software [4]. Then, those parameters were used during the experimental procedure to produce Al-Hf coatings at low temperature under atmospheric pressure. The effect of a diffusion heat treatment also was studied in order to promote the phase transformation from Fe_2Al_5 (brittle phase) to lower Al content phases such as FeAl and Fe_3Al (for better mechanical behavior and corrosion resistance).

Experimental details

Composition of material. The chemical composition of the ferritic steel used as the base material for Al-Hf diffusion coating is presented in Table 1. Samples (10 mm x 20 mm x 3mm) were polished from 240- grit SiC paper up to 600 grit SiC paper and then ultrasonically cleaned in alcohol, dried and weighed prior to the coating experiment.

Table.1 Composition of the ferritic steel (wt%)

Steel	Fe	Cr	V	Ni	Mo	Mn	Si	Nb	Cu	Al	C	N
HCM-12A	83,5	12,5	0,21	0,34	0,36	0,54	0,25	0,05	0,85	0,01	0,09	0,06

Coating procedures.

1 Thermodynamic calculations. Thermodynamic study of gas precursors (composition, partial pressure) and solid phases obtained during CVD processing were performed using Thermocalc [*4*] computer program to determine feasibility of metal deposition, and provide guidelines to optimise the deposition conditions. The calculations were based on the Gibbs free energy minimizations and mass conservation rule, in combination with the SSUB3 and SSOL2 databases for gaseous and solid phases, respectively.

2 Coating deposition. The Al-Hf coatings were formed using CVD-FBR. A schematic diagram of the CVD-FBR system used in this study is described elsewhere [*5*]. The reactor consisted of a quartz tube with an internal diameter of 3,5 cm and was heated by radiation by using an external furnace. The bed used was composed of a mixture of 10 % wt Al powder of 99.5 % of purity and ≤ 400 µm particle size as donor; the hafnium powder used was 250 µm in diameter and 99% in purity. The powder mixture was fluidized by Ar gas (99.999 purity), and hydrogen chloride (HCl) was used as an activator to generate an Al precursor. The imput $Ar_{(g)}$ entering in the reactor contained 24 vol. % H_2 and 1,5 vol. % HCl./

After deposition of the CVD-FBR coatings, a diffusion heat treatment was performed under argon flow at 700 º C for 4 hours, followed by cooling to room temperature under an atmosphere of Ar gas.

Oxidation condition. For the oxidation studies, the specimens were exposed to a 100% vol H_2O atm. A schematic diagram of the closed-loop laboratory rig employed is shown in Fig. 1. Prior to testing, air was displaced from the testing chamber by means of N_2 which wass kept flowing while heating up to the test temperature (approximately 650°C). When the test temperature was achieved, the N_2 flow was cut and the steam flow was switched on. Before removal of samples, the furnace was cooled to about 100°C under N_2. The reheat cycle (from 100°C to the test temperature) is also carried out under N_2. Samples were removed after 1000 hours for metallographic analysis.

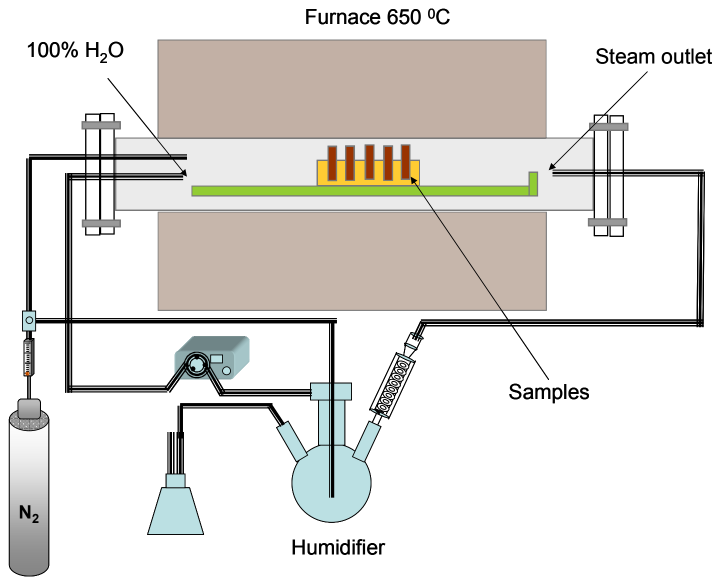


Fig. 1. Experimental setup for oxidation studies in steam environment.

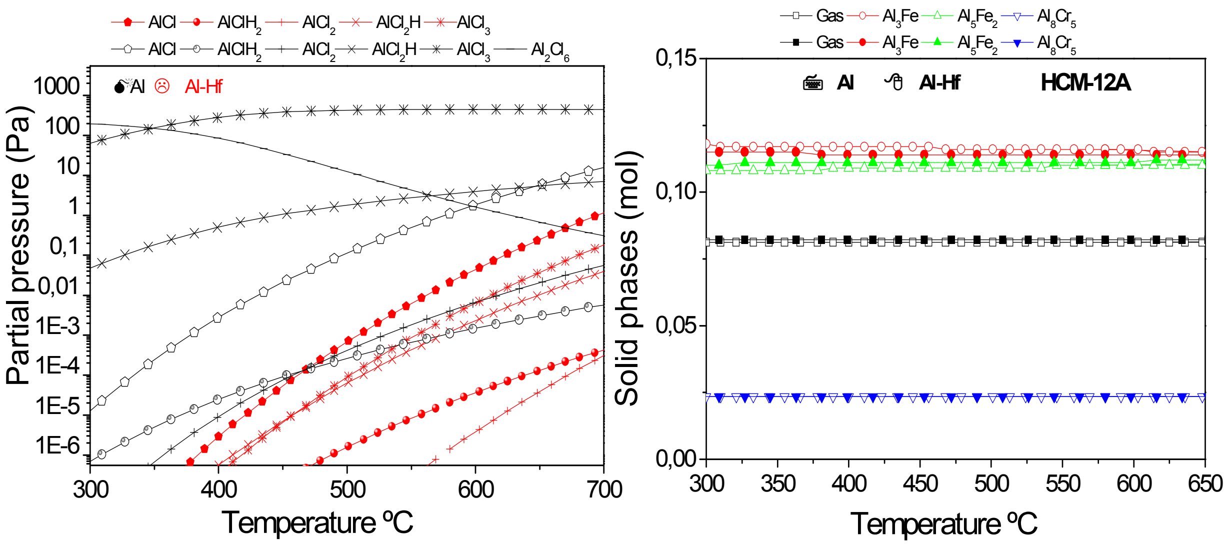
Characterisation techniques. The characterization of the coated specimens was carried out using metallographic preparation followed by scanning electron microscopy (SEM JEOL JM-6400), and energy dispersive X-ray spectroscopy (EDS) analysis. The structures of the intermetallic compound layers were identified by X-ray diffractometer (PHILIPS X´PERT MPD) using monochromatic Cu K_α radiation. The X-ray diffraction (XRD) measurements were performed using a goniometer at a scanning range of $0<2\theta<90$ and step size of 1º, at 45kV and 40 mA with a collimator with 0.2 mm slit.

In order to evaluate the steam oxidation rate, the weight gain of each specimen was measurement during the steam oxidation test by using a precision balance with an accuracy higher than 0,1 mg. Also, the cross section of the samples of the oxidized specimen was observed by using SEM/EDS. The oxides formed in steam were identified by an X-ray diffraction technique.

Results and discussion

Thermodynamic calculations. Thermodynamic calculations performed using the Thermocalc [4] program were carried out to estimate the gas phase and solid phase composition in the equilibrium conditions after the aluminization process. Fig. 2a shows the gaseous precursors formed in the system Al and Al-Hf. The addition of Hf to the system (Fig. 2a) had two main effects: a change in the partial pressures of the Al precursors ($AlCl_3$, Al_2Cl_6 and AlCl) and an inversion of the order of the formation of the precursors. In this case, the partial pressure of AlCl was higher than $AlCl_3$.

Fig. 2b shows the equilibrium composition of the compounds formed on the surface of a ferritic steel as a function of temperature. The most stable phases in the temperature range between 300-650^{0}C were the intermetallic compounds Fe_2Al_5 and $FeAl_3$. Thermodynamic estimations suggested that the formation of Al_8Cr_5 also could be expected.



a) b)

Fig. 2. Thermodynamic calculations for the gaseous and solid phases formed at equilibrium conditions as a function of temperature

Coatings characterization

<u>XRD analysis.</u> XRD patterns for the Al coating on HCM-12A steel were recorded before and after heat treatment. Before heat treatment the characteristic peaks of the compounds $FeAl_3$, Fe_2Al_5 and FeAl were observed. The presence of these phases is consistent with the aforementioned EDS analysis. XRD patterns after heat treatment show that the composition of the coating had changed and was mainly composed of Fe_2Al_5 and FeAl.

<u>SEM and EDS analysis.</u>

SEM and EDS analysis of samples without diffusion heat treatment. Fig. 3 a) shows cross-sections of the Al-Hf coatings on the ferritic steels before any diffusion heat treatment, which indicate that the coating was homogeneous. Furthermore, the thickness of the Al-Hf coatings was approximately 10 µm. This Fig. also shows the corresponding composition of coatings as a function of depth. These line profiles show that the coatings mainly consisted of Al, Fe and Cr. As expected from the equilibrium phase diagram [6], the coating consisted of 3 layers; an inner layer of Fe_2Al_5, an intermediate layer of a mixture of intermetallic compounds (Fe_2Al_5 and $FeAl_3$), and an outer layer of $FeAl_3$. The structures of these phases can contain up to 6.4-6.2 at % of Cr without altering their lattice parameters [7]. Therefore, it can be assumed that the Cr in the coatings was in solid solution. Growth of the aluminum coating occurred mainly by mechanism of the reaction diffusion.

SEM and EDS analysis of samples with diffusion heat treatment. In order to promote the transformation of the as deposited $FeAl_3$ and Fe_2Al_5 coatings to into Fe_3Al and/or FeAl to improve the mechanical properties of the coating, a diffusion heat treatment was conducted on deposited samples. The heat treatment was performed under flowing argon at 700°C for 4 hours, followed by cooling to room temperature under an **Ar** gas atmosphere.

Fig. 3 b) shows cross-sections of the aluminide coatings on HCM-12A after the diffusion heat treatment. The vertical line shows the region where the EDS line scan analysis was performed. In this Fig., two regions can be clearly distinguished: an outer grey dark region with some round precipitates (lighter in color) and an inner interdiffusion zone. EDS line analysis revealed that the coatings mainly consisted of Fe, Cr and Al. The coating consisted of 4 layers. The thickness of the outer layer was 5,3 µm, and the line profile showed it to be Fe_2Al_5 containing precipitates with Fe, Al, Cr with a similar stoichiometric ratio to FeAl. Overall, the four phases corresponded to the diffusion zone. The occurrence of AlN precipitates was observed in the alloy immediately beneath the coating.

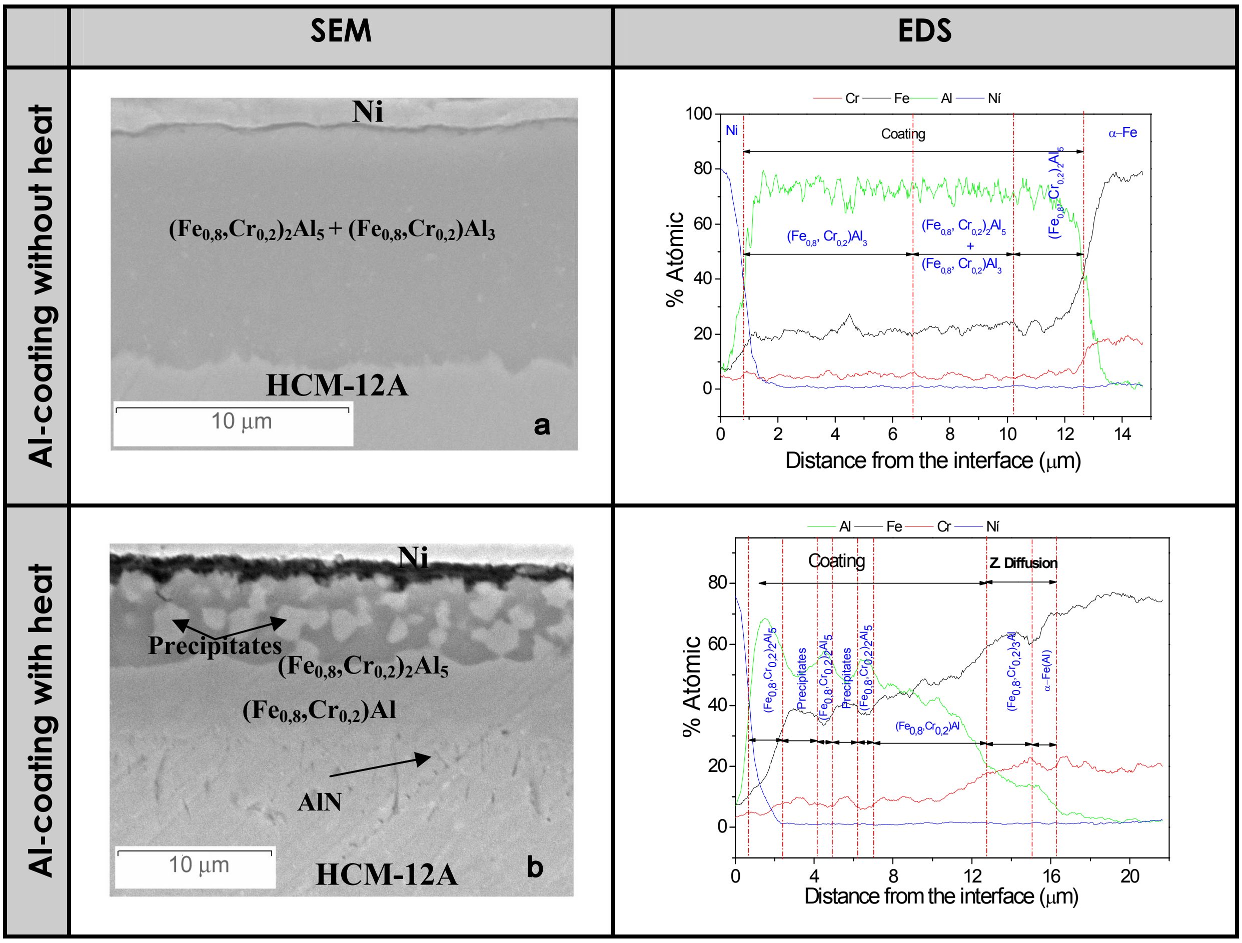


Fig. 3. SEM micrograph of the cross-section of **Al** coatings deposited onto P-91 and corresponding EDS line profile a) without heat treatment and b) with heat treatment.

Steam oxidation testing. Fig. 4 shows the mass change results for steam oxidation testing in 100% H_2O at 650°C for 3000 h. The uncoated sample of HCM-12A experienced a large increase in weight compared with the coated sample. To characterize the microstructure of the oxide scale and the distribution of elements, a cross-sectional analysis by SEM/EDS was made for both samples. The SEM analysis of the samples after 1000 h of oxidation under these conditions showed that the oxide scale formed on the uncoated sample had a thickness of about 26 µm, and was compact and homogeneous (Fig. 5a). According to the line analyse, the outer scale mainly consisted of Fe_3O_4 with an inner scale of $(Fe,Cr)_2O_3$, identified by X-ray diffraction. In contrast, the aluminized specimens after 1000 h of exposure (Fig. 5 b), formed a very thin outer oxide scale (about 1 µm), which consisted of α-Al_2O_3. The inner coated consisted of FeAl and Fe_3Al.

The results showed that, in the uncoated samples the oxide scale consisted of $(Fe,Cr)_2O_3$ and Fe_3O_4. According to results reported in the in the literature, the possible mechanism of growth of this scale is due at the formation initially of a layer with a high Cr content $(Fe,Cr)_3O_4$ and as a consequence of the interaction of this scale with the steam, the formation of the volatile species produces the breakdown of this protective scale. Also, in the sites where breakdown occurs the formation of the Fe_3O_4 is favored. As a consequence of the local breakdown, fast growth of an Fe_3O_4 scale takes place. The rapid outward cation diffusion leads to inward transport of vacancies which condense locally into large voids. More pores and cracks are formed areas of rapidly- growing scale, probably due to vacancy condensation or a dissociation processes in the scale. Therefore, the morphology of the scale formed is composed of two layers: an inner layer of spinel $(Fe,Cr)_3O_4$, and an outer layer of Fe_3O_4. Our results for uncoated samples exposed at the 100 % steam atmosphere after the 1000 hours of testing correspond to this scenario.

The samples coated with Al-Hf exhibited significantly-improved the resistance against steam oxidation. This could be explained by the formation of a thin scale of α-Al_2O_3 on the coating. The degradation of the coating was causd mainly by inward diffusion of Al into the substrate. Therefore, it is suggested that a possible mechanism of degradation of this coating under these conditions is due to two simultaneous processes. The first process consists of formation of α-Al_2O_3 and the second process is the transformation of the Fe_2Al_5 coating into FeAl, Fe_3Al along with formation of precipitates of AlN due a process of outward diffusion of Fe and Cr, diffusion of and Al inwards. This behaviour is similar at observed by Aguero *et al.*[9]. in slurry aluminide coatings for steam turbine components.

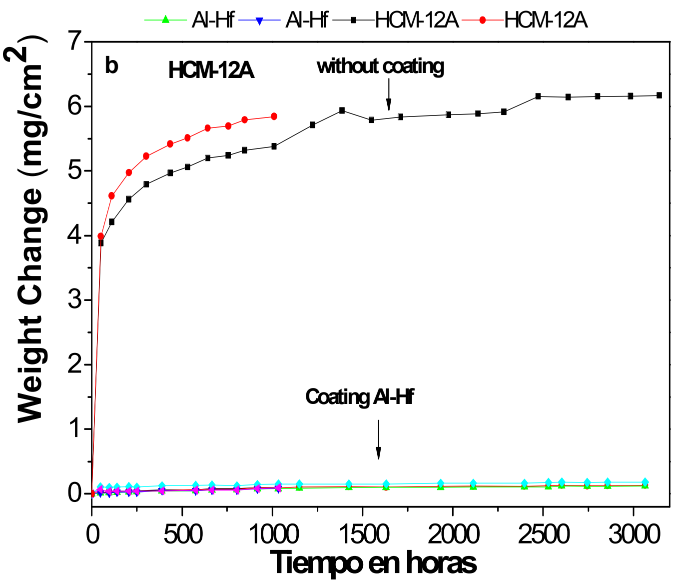


Fig. 4. Weight variation as a function of time for Al-coatings and P-91 steel under steam oxidation conditions at 650°C.

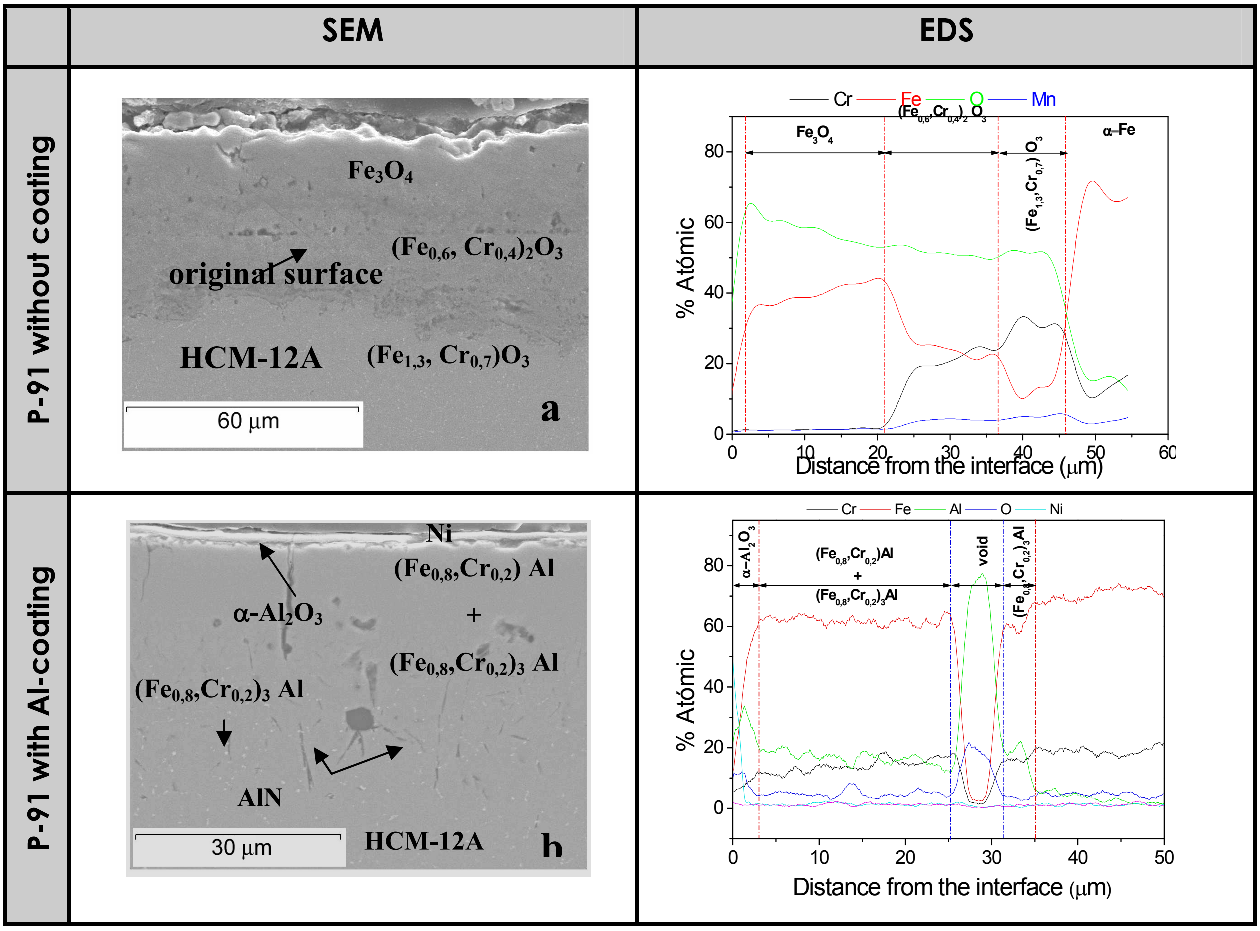


Fig. 5. SEM micrograph of the cross-section and corresponding EDS line profile of specimen oxidized for 1000 h at 100 % H_2O at 650°C. a) Uncoated samples and b) Al-Hf coating with heat treatment.

Conclusions

The results obtained have demonstrated that Al-Hf coatings have a beneficial effect in the protection of the ferrtic steel HCM-12A against oxidation in steam at 650°C. This fact makes such coatings very interesting for future applications in power plant. The Hf have not been found on the SEM cross sections, probably due of its small amount.

The excellent behaviour observed in the samples with Al-Hf was due to the formation of think a layer of α-Al_2O_3.

The main advantages of CVD-FBR deposition of Al-Hf coatings are that it can be realized at temperatures below 600°C, in short times, at a low cost without affecting the microstructure of the materials.

The Hf have not been found on the SEM cross sections, probably due of its small amount.

Aknowledgements

The authors want to express their gratitude to the Ministerio de Educación y Ciencia for the financial support of this work under contract ENE-2005-08494-C02-02

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