

ARTICLE

TGA-MS study of steam oxidation resistance of HCM12A steel at 750 and 800 °C

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Initial oxidation stages of the ferritic/martensitic HCM12A steel at 750 and 800 °C in Ar + 40% H₂O for 190 h were studied in a closed steam loop by means of mass spectrometry (MS) and thermogravimetric analysis (TGA). TGA measures verified that mass gained by the HCM12A oxidized steel at 750 °C was up to two times lower than for HCM12A oxidized steel at 800 °C. Thermo-Calc program under same oxidation conditions of experiments was used for study of some theoretical oxidation simulations. The MS measurements at 750 °C of the HCM12A steel for 190 h indicated the presence of low intensity (in order of ppm) volatile species Mn(OH)₃(g), Mn(OH)₇(g), and CrOOH(g). While the HCM12A oxidized steel in steam at 800 °C and under same oxidation conditions emitted only a volatile CrOOH(g) species of double intensity. Therefore, it confirmed that the loss and rupture of the chromium scale of the steel can accelerate when the oxidation temperature increases. The morphology, composition, and structure of samples by scanning electron microscopy (SEM), electron back-scattered diffraction (EBSD), X-ray energy dispersive spectrometry (EDAX), and X-ray diffraction (XRD) are described.

KEYWORDS

ferritic/martensitic steel, mass spectrometry, steam oxidation, thermogravimetry measurements, volatile species

1 | INTRODUCTION

The development and construction of steam-electric power generation systems have led to a revival in research on the effects of oxidation in steels and alloys, particularly chromium-containing steels. Ferritic steels have excellent resistance to oxidation and austenitic steels have high hardness and strength. On the other hand, martensitic 9–12% chromium steels are used to manufacture important components in steam power plants such as rotors, piping and valve bodies due to their low thermal expansion, high thermal conductivity, and acceptable corrosion properties.^[1,2] Ferritic–austenitic steels are the most commonly used substrates at high temperatures of up to 600 °C and they are candidates for future coal combustion power plants. Many researchers^[3–5] have reported oxidation kinetic results for ferritic/

martensitic steels with 9–12% Cr, under different oxidation conditions; temperatures, pressure, and diverse atmospheres (O₂, air, water steam, N₂, Ar, as percentages of O₂–H₂O, etc.). These steels have been studied as structural materials for energy industry applications. Thus, considerable attention has been paid to the influence of steam at high temperatures on oxidation behavior of Fe, Cr, and FeCrNi alloys.^[6–8]

In order to find more resistant steels for steam turbines at temperatures above 650 °C, HCM12A steel (ASME P122)^[9] is an advanced nominal 12 Cr ferritic/martensitic steel designed for higher temperature operation, that has attracted increasing attention for application in core components in Generation IV Nuclear Energy System. The benefits of this steel over supercritical water (SCW) are the good results to improve fuel deposits and reduce harmful gas emissions.^[10]

Tan et al.^[11] carried a study of SCW (supercritical water) oxidation of HCM12A steel at 500 °C, 25 MPa from 192, 384, and 576 h, and two levels of oxygen partial pressure by means of gravimetry, SEM/EDAX, XRD, and EBSD. They found that the oxide scale of HCM12A steel oxidized at low oxygen pressure contained magnetite (Fe_3O_4)/spinel (FeCr_2O_4) phases, and high-oxygen exposed steel contained a oxide scale of magnetite/spinel, hematite (Fe_2O_3) and corundum (Cr_2O_3 , $(\text{Fe,Cr})_2\text{O}_3$) phases. Thus, these results obtained in this study indicate that the formation of phases and porosities in the oxide scale depended upon oxygen potential. Moreover, others researchers^[12,13] had reported results of XRD analysis of HCM12A steel oxidized in high oxygen content. They confirmed good oxidation resistance properties of the HCM12A. Thus, several crystalline phases such as the magnetite (Fe_3O_4) and the mixed spinel FeCr_2O_4 were observed. Additionally, they observed other thin layers such as the hematite (Fe_2O_3) and the corundum type protective layers (Cr_2O_3 , $(\text{Fe,Cr})_2\text{O}_3$). Some researchers have reported greater growth of protective oxide scale at 650 °C when hydrogen is supplied to the steels.^[14,15] Similar morphology, structure, and thickness were found in the oxide scales, regardless the nature of oxidation process (air or steam). According to models of hydrogen-accelerated oxidation, previously proposed by many researchers,^[16,17] a mixed spinel type, $(\text{Fe,Cr})_3\text{O}_4$ works as a key phase of the steel to prevent accelerated growth of oxide scale during steam oxidation.^[15,18,19]

Pérez and Castañeda^[20] presented an earlier study on P91 steel with and without AlFe-slurry coating oxidized at 650 °C in Ar + 80% H_2O atmosphere. After 100 h of oxidation of uncoated P91 steel, volatile species such as Cr(g), $\text{CrO}_2(\text{g})$, $\text{CrOOH}(\text{g})$, $\text{CrO}_2(\text{OH})_2(\text{g})$, $\text{Cr}(\text{OH})_6(\text{g})$, $\text{FeOOH}(\text{g})$, $\text{Fe}_{0.947}\text{O}(\text{g})$, $\text{Fe}_2\text{O}_3(\text{g})$, CO, CO_2 , Mo(g), and $\text{HNi}(\text{g})$ were detected by MS analysis. Whereas on the coated P91 steel after 200 h of oxidation, species such as Al(g), AlO(g), and $\text{FeOOH}(\text{g})$ were observed. By thermogravimetric measurements it was found that uncoated steel loses protection when compared to coated samples because uncoated oxidized P91 steel shows a higher rate of oxidation due to the breakdown of chromia scales, as verified by mass spectrometry. MS also revealed the presence of the $\text{CrO}_2(\text{OH})_2(\text{g})$ species during oxidation. Furthermore, an XRD analysis of the oxide scale found layers such as Fe_2O_3 , Fe_3O_4 and a mixed spinel of iron and chromium (FeCr_2O_4).

Castañeda et al.^[21] have presented MS results of other experimental work of steam oxidation of the P91 steel with and without Al-CVD-FBR coating at 650 °C in Ar + 40% H_2O steam for 190 h. They reported presence of some volatile species of low intensity (in order of ppm) at different oxidation times, e.g., $\text{Fe}_2\text{O}_3(\text{g})$, $\text{Cr}(\text{OH})_2(\text{g})$, $\text{Cr}_2\text{O}(\text{g})$, $\text{Cr}_2\text{O}_2(\text{g})$ for 75 h; $\text{FeO}(\text{g})$, $\text{Cr}(\text{OH})_2(\text{g})$, $\text{CrO}_3(\text{g})$, $\text{CrO}(\text{OH})_3(\text{g})$, $\text{Cr}_2(\text{OH})(\text{g})$ for 100 h; $\text{Cr}(\text{OH})_3(\text{g})$, $\text{Fe}(\text{OH})_3(\text{g})$,

$\text{Cr}_2(\text{OH})(\text{g})$ for 125 h; $\text{Fe}_2\text{O}_3(\text{g})$, $\text{FeOOH}(\text{g})$, $\text{CrO}_3(\text{g})$, $\text{Cr}_2(\text{OH})(\text{g})$ for 150 h; $\text{Fe}_2\text{O}_3(\text{g})$, $\text{Mn}(\text{OH})_3(\text{g})$, $\text{Fe}(\text{OH})_3(\text{g})$, $\text{CrO}_4(\text{g})$ for 175 h; and finally, $\text{Fe}_2\text{O}_3(\text{g})$, $\text{CrO}(\text{OH})_2(\text{g})$, $\text{Fe}(\text{OH})_3(\text{g})$, $\text{NiCrO}(\text{g})$ for 190 h. However, no volatile species were observed before 50 h of oxidation. In addition, by XRD analysis, they observed that the oxide scale was composed of structures of two phases; the cubic magnetite (Fe_3O_4) and the rhombohedral hematite (Fe_2O_3).

Ebbinghaus^[22] studied the oxidation thermodynamics of chromium at high temperature and found three gaseous chromium oxides and twelve gaseous chromium oxyhydroxides. Chromium volatility was assessed during waste incineration processes from 800 to 1600 K and at different steam and oxygen pressures: $P(\text{H}_2\text{O}) = 0.0125$ to 0.2 atm and $P(\text{O}_2) = 1.17 \times 10^{-6}$ to 0.2 atm. The work concluded that for equilibrium oxidation calculations, a fraction of $\text{CrO}_2(\text{OH})_2(\text{g})$ was the dominant species, with small contributions from $\text{CrO}(\text{OH})_3(\text{g})$, $\text{CrO}_3(\text{g})$, $\text{CrO}_2\text{OH}(\text{g})$, and $\text{CrO}(\text{OH})_2(\text{g})$, when fixing oxygen (0.10 atm) and water (0.10 atm) pressures at high temperature over $\text{Cr}_2\text{O}_3(\text{s})$. Moreover, predicted chromium volatility was maximized when including $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ in equal quantities. With $\text{O}_2(\text{g})$ or $\text{H}_2\text{O}(\text{g})$ at low pressures, the overall chromium species pressure was dramatically reduced. In other investigations, some volatile species have been identified such as $\text{CrO}_2\text{OH}(\text{g})$ ^[23,24] and $\text{CrO}_2(\text{OH})_2(\text{g})$ ^[25,26] after volatilizing chromium from samples of Cr(s) and $\text{Cr}_2\text{O}_3(\text{s})$ at high temperature in presence of air and water steam.

A main goal of work is to verify the advantages of HCM12A steel against critical oxidation at 750 and 800 °C in Ar + 40% H_2O atmosphere for 190 h. On the other hand, other objectives were to find a direct relationship between the theoretical simulations and the TGA-MS experiments and verify the formation of volatile species (inorganic oxyhydroxides) during the initial steam oxidation period of HCM12A steel. Moreover, in the present work, the results of HCM12A steels oxidized in the work are compared with results of other ferritic/martensitic steels oxidized under same conditions.

2 | EXPERIMENTAL

Oxidation tests of ferritic/martensitic HCM12A steel (supplied by Sumitomo Metal Industries) were carried out in this work. The steel chemical composition was Fe = 82.858, Cr = 12.5, Mo = 0.36, Mn = 0.54, Si = 0.25, C = 0.07, Ni = 0.34, V = 0.21, Al = 0.01, Nb = 0.05, N = 0.06, S = 0.002, W = 1.90, and Cu = 0.85 (in wt%). HCM12A steel was cut and polished with SiC emery papers from 100 to 1000 meshes. The samples were cleaned with acetone in an ultrasonic bath for 10 min followed by a drying process at 100 °C for 15 min.

Oxidation experiments and thermogravimetric measurements were performed using a thermobalance (sensitivity of 10^{-7} g) with a symmetrical thermoanalyzer (SETARAM-model TAG 16). The procedure of these oxidation tests was described in previous publications.^[20,21] The specimens at 750 and 800 °C in Ar + 40% H_2O for 190 h were oxidized. Simultaneously the study of volatile species emanating from samples during oxidation was made by placing a Quadrupole Mass Spectrometer QMS 422 (PFEIFFER VACUUM instruments) very close to the test sample. As a preliminary procedure, the background of the TGA system (before inserting the sample) was measured under similar experimental conditions, and the respective data were subtracted from the MS results. MS figures show lines of volatile species for the samples studied that appear at different times and reference lines of the oxidation atmosphere. The volatile species results of the samples were studied and compared with other species of the literature and with some MS databases.^[22,27–32] The Thermo-calc program (Software AB: Foundation of Computational Thermodynamics 1995–2003, Stockholm, Sweden) was used for the theoretical simulation of oxidation at equilibrium from 500 to 900 °C. The input data for the oxidation simulation were the same for all the experiments. Our initial database was the results of simulations and these were interpreted with the literature. Microstructure characterization of specimens was made by means of a Philips X'Pert diffractometer, using Cu K α (1.54056 Å) radiation; in (θ -2 θ) angle mode. Morphology and composition of the specimens were analyzed by scanning electron microscopy (SEM) using a JEOL-JSM 6400 microscope equipped with an energy dispersive X-ray analysis (EDAX) detector and operated at 20 KV. Images of surface and cross section were taken by means of secondary electron emission and by electron back-scattered diffraction (EBSD).

3 | RESULTS AND DISCUSSION

Thermogravimetric measurements of the mass change as a function of oxidation time of HCM12A steel at 750 and 800 °C in Ar + 40% H_2O atmosphere for 190 h are shown in Figure 1. HCM12A steel oxidized at 750 °C gained mass of around 0.11375 mg/cm² (curve a), while the same steel oxidized at 800 °C gained around 0.25252 mg/cm² (curve b). The results corroborated that both steels oxidized gained little amount of mass. It is probable that the protection against steam oxidation of HCM12A steel was due to the great percentage of chromium in their composition. The chromium in contact with oxygen of the steam formed protective layers such as chromia (Cr_2O_3) and another possible mixed spinel (Fe, Cr, O). Protective layers that helped prevent or to retard steam oxidation.

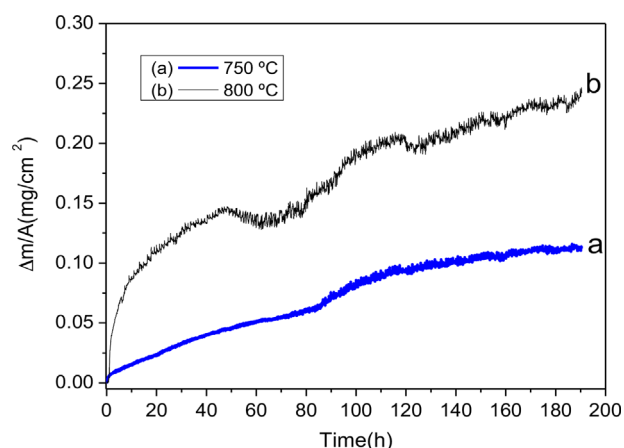


FIGURE 1 Mass gain versus oxidation time of the HCM12A steel at two temperatures in Ar + 40% H_2O for 190 h: (a) 750 °C and (b) 800 °C. [Color figure can be viewed at wileyonlinelibrary.com]

3.1 | Theoretical simulation of steam oxidation of HCM12A steel

The thermodynamic calculations of steam oxidation of HCM12A steel were made with the Thermo-calc program under similar steam condition of the experiments and temperature range from 500 to 900 °C. These calculations are based on the minimization code of Gibbs free energy and the rule of mass conservation in accordance with the database provided by the program and the bibliography.^[28,29] The oxidation simulations were calculated for a steam atmosphere on the steel, aiming to find possible solid phases and gaseous species that could be formed under these oxidation conditions. These theoretical results were subsequently compared with the experimental results of HCM12A oxidized steel.

Figure 2 shows simulation results of solid phases of HCM12A steel oxidized in Ar + 40% H_2O atmosphere from 500 to 900 °C. The calculations showed the presence of FeO

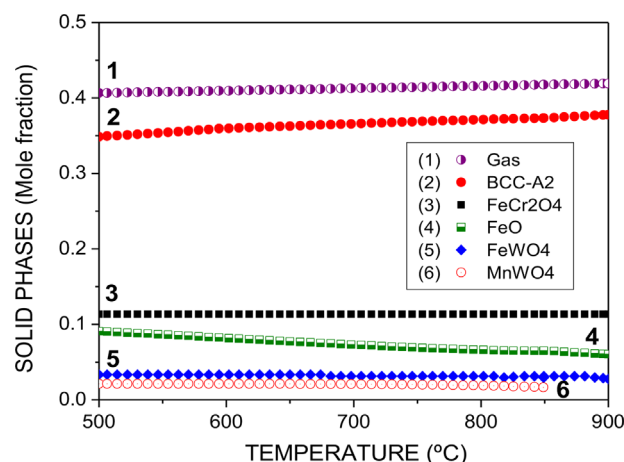


FIGURE 2 Solid phases calculated by oxidation thermodynamic simulation in Ar + 40% H_2O of HCM12A steel from 500 to 900 °C. [Color figure can be viewed at wileyonlinelibrary.com]

oxide (wüstite), Cr_2FeO_4 mixed spinel, the mixed oxides FeWO_4 and MnWO_4 , and the alloy BCC-A2 with composition of $\text{Fe}_{0.7098}\text{Cr}_{0.2049}\text{W}_{0.0022}\text{Mn}_{0.0017}\text{Mo}_{0.0015}$. The oxide of Fe and the mixed spinel are the most stable solid phases that they can form. The results predicted that the HCM12A steel is affected by these steam oxidation conditions, although the effect is less aggressive compared to the damage caused to other ferritic steels such as P91, P92, FB2A.^[33–35] According to the results during simulation, the predominant presence of FeCr_2O_4 spinel layer (mixture of chromia (Cr_2O_3) + wüstite (FeO)) on HCM12A steel indicates better protection against these steam oxidation conditions. According of results, the high negativity of total Gibbs free energy^[27–29] calculated of the oxidation system ($\Delta G \sim -16348$ kJ/mol) has guaranteed a high thermodynamic probability of formation of the solid phases aforementioned. Additionally, the figure shows other lines of the oxidation conditions such as gases Ar, H_2O , and O_2 .

Figure 3 shows the results of the calculations for the gaseous species that could appear during the oxidation of HCM12 steel for the temperature range of 500–900 °C. This graph represents the partial pressure (Pa) of the gaseous species as a function of the oxidation temperature. The figure shows some species of oxides, hydroxides, and oxyhydroxides of Fe, Cr, Ni, Mn, and Mo, such as $\text{H}_2\text{WO}_4(\text{g})$, $\text{Fe}(\text{OH})_2(\text{g})$, $\text{HMn}(\text{g})$, $\text{H}_2\text{MoO}_4(\text{OH})_2(\text{g})$, $\text{Mn}(\text{g})$, $\text{Fe}(\text{g})$, and $\text{Fe}(\text{OH})(\text{g})$ for the partial pressure range from 10^{-16} to 10^{-8} Pa. Thus, other species as $\text{Cr}(\text{OH})_2(\text{g})$, $\text{Cr}(\text{OH})_3(\text{g})$, $\text{CrOOH}(\text{g})$, $\text{FeH}(\text{g})$, $\text{FeO}(\text{g})$, $\text{Fe}(\text{OH})_2(\text{g})$, $\text{Mn}(\text{OH})(\text{g})$, and $\text{MoO}(\text{OH})_2(\text{g})$ at a partial pressure between 10^{-16} and 10^{-14} Pa. Finally, the figure shows other lines such as $\text{H}_2(\text{g})$, $\text{Ar}(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{OH}(\text{g})$, and $\text{H}(\text{g})$, corresponding to initial oxidation conditions. According to the results, the low emission of volatile species of chromium and iron (oxides, hydroxides, and oxyhydroxides) of HCM12A steel during the test proves to us the good properties against steam oxidation of this steel.

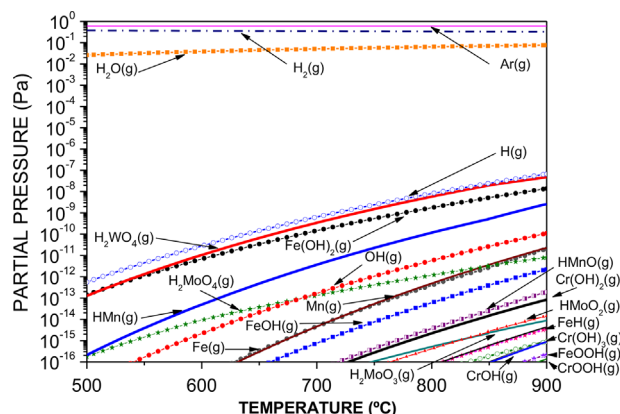


FIGURE 3 Partial pressure of gaseous species calculated by thermodynamic simulation of HCM12A steel in Ar + 40% H_2O from 500 to 900 °C. [Color figure can be viewed at wileyonlinelibrary.com]

3.2 | Oxidation tests

Figure 4a–c shows three representative mass spectra of HCM12A steel oxidized at 750 °C in steam for 25, 50, and 150 h. Table 1 shows all mass spectrometry results made

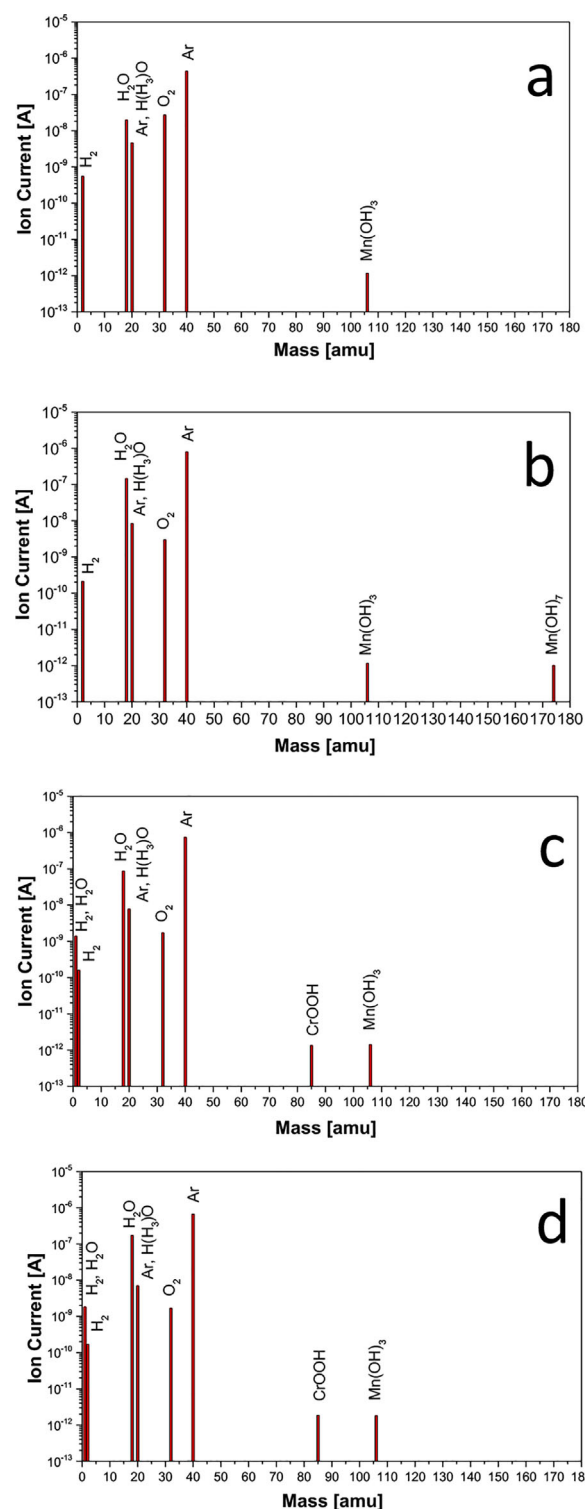
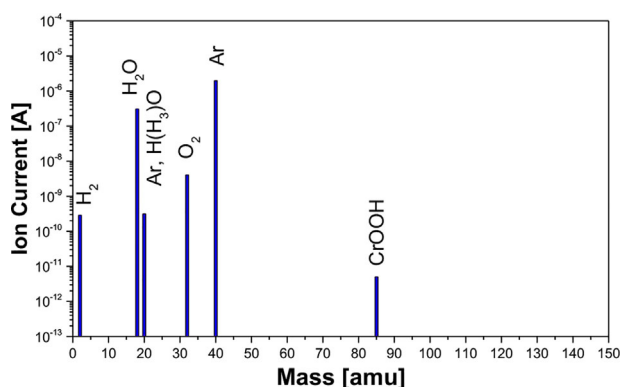


FIGURE 4 Mass spectra at different oxidation times of HCM12A steel at 750 °C in Ar + 40% H_2O : (a) 25 h, (b) 100 h, (c) 150 h, and (d) 190 h. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Mass spectrometry analysis made at different oxidation times in Ar + 40% H_2O of HCM12A steel for 750 and 800 °C

Temperature (°C)	Volatile species/time								
	4 h	25 h	50 h	75 h	100 h	125 h	150 h	175 h	190 h
750	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃	Mn(OH) ₃
			Mn(OH) ₇	Mn(OH) ₇	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH
800	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH	CrOOH

during some oxidation times of the steel i.e., 4, 25, 50, 75, 100, 125, 150, 175, and 190 h. Volatile species of small intensity (between 1 and 3 ppm) of manganese and chromium such as the hydroxides $\text{Mn(OH)}_3(\text{g})$ and $\text{Mn(OH)}_7(\text{g})$, and the oxyhydroxide $\text{CrOOH}(\text{g})$ were observed, where $\text{Mn(OH)}_3(\text{g})$ was the predominant volatile species. In addition, the $\text{CrOOH}(\text{g})$ species was observed from 100 h of oxidation. The small amount and intensity of the volatile species emitted during oxidation of HCM12A steel verified the high oxidation resistance of the steel. A representative mass spectrum of HCM12A oxidized steel at 800 °C for 190 h is shown in Figure 5. Only a common and predominant species of chromium i.e., $\text{CrOOH}(\text{g})$ was observed throughout the test (Table 1). Furthermore, a species of chromium of double intensity in comparison with the species was observed during steam oxidation of HCM12A steel at 750 °C. Although the amount and intensity of chromium gaseous species observed of HCM12A steel oxidized at both temperatures were lower compared to species emitted by other oxidized ferritic steels under the same conditions.^[21,34,35] These results verified the high resistance to steam oxidation of HCM12A steel compared to other steels. With TGA-MS, we verify the good behavior of the steel and the formation of volatile species (inorganic oxyhydroxides) during the initial steam oxidation period of HCM12A steel; where few Mn and Cr volatile species were observed. It is known that the diffusion of Cr and Mn takes place on grain boundaries. These diffused

**FIGURE 5** A representative mass spectrum of HCM12A oxidized steel at 800 °C in Ar + 40% H_2O for 190 h. [Color figure can be viewed at wileyonlinelibrary.com]

elements form protective layers like chromia or a certain mixed spinel (Fe, Cr, Mn, O) together with the Fe of the steel, these layers help to avoid or retard steam oxidation of steel. Thus, this apparent loss and degradation of Mn and Cr may be due to volatilization during the formation of protective layers of either chromia or some spinel, and possibly when the oxidation temperature increases (800 °C). Additionally, at 800 °C, the low Mn concentration of the steel is rapidly depleted and/or the fast formation of chromia avoids loss of other elements by volatilization.

Figure 6a–d shows micrographs generated by detection of secondary electron emission and EBSD images of the surface and the cross section of HCM12A oxidized steel at 750 °C in Ar + 40% H_2O for 190 h. The SEM image of the surface shows some “oxide islands” or crust of oxidation up to 100 μm of diameter (Figure 6a). The crusts were composed of many small nodules that at higher magnifications showed clusters compressed of leaves or a structure of bush form (Figure 6b). EDAX analysis of surface of an oxide node of this sample verified a composition of Fe = 61.85, Cr = 2.19, O = 28.48, Mn = 3.29, C = 3.25, and Cu = 0.39 (wt%). In addition, other image at similar magnifications of flat part of the oxide scale (Figure 6c) shows many grains of small crystals and various sizes, between 0.15 and 1 μm in diameter. EDAX analysis of a small area of flat part of the oxide confirmed the composition of Fe = 39.24, Cr = 17.89, O = 27.46, Mn = 11.98, Si = 0.38, C = 1.25, V = 0.32, and Cu = 1.06 (wt%). It is likely that the metallic elements (Cr, Fe, Mn) of the steel in contact with oxygen of the steam form oxides such as Cr_2O_3 , the mixed spinel FeCr_2O_4 and another possible mixed spinel (Fe, Cr, Mn, O). Layers that helped protect the steel against steam oxidation. Figure 6d,e shows EBSD images of cross section of HCM12A oxidized steel at 750 °C. One first micrograph shows two oxide nodules or “oxide islands” with different contrasts, with great porosity and sizes of 20 and 35 μm of thickness (Figure 6d). The second micrograph made at high magnification of the cross section of an oxide node (Figure 6e) shows several cracks below the island/crater oxide interface. Moreover, we observed a node of 35 μm of thickness, where around of 18 μm correspond to the “oxide island” and around of 17 μm to the “oxide crater.” An elemental mapping of composition of cross section of oxide node of HCM12A oxidized steel at 750 °C (Figure 7) has corroborated the interdiffusion of the predominant elements (Fe, Cr, and Mn) of the steel and the

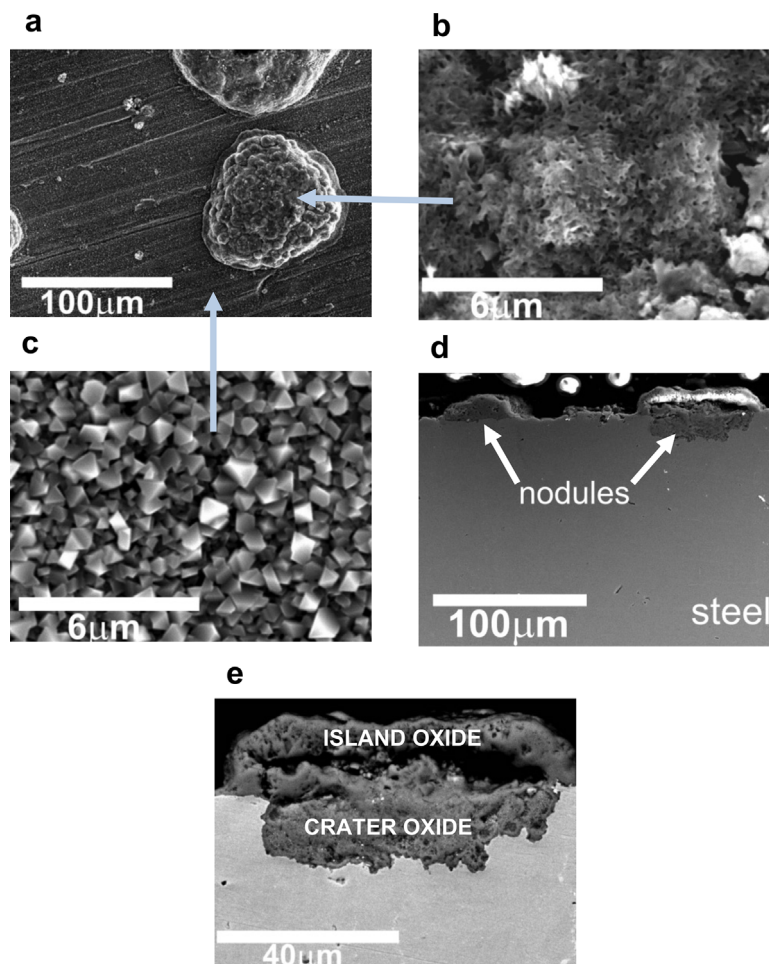


FIGURE 6 Micrographs at different magnifications of oxide scale of HCM12A steel at 750 °C in Ar + 40%H₂O for 190 h; SEM images of surface: (a) the oxide scale, (b) morphology of an oxide node, and (c) the flat part of the oxide scale; EBSD images of a cross section of the oxide scale: (d) observation of two oxidation nodules and (e) an oxide node. [Color figure can be viewed at wileyonlinelibrary.com]

oxygen inside of the sample. Thus, the distribution of elements of composition of the oxide node and the dimensions of the areas of “oxide island” and “oxide crater” aforementioned were verified.

The EDAX analysis results on four points of a cross section of an oxide node of HCM12A steel oxidized at 750 °C is shown in Figure 8 and Table 2. High concentrations of Fe and O and low concentrations of Cr and Mn were observed in the top part (points 1 and 2 in Figure 8). Meanwhile, higher concentration of Fe, Cr, O and low concentrations of Mn, V, W, Ni, and Cu were observed in the inner part (point 3 in Figure 8). Likewise, high concentrations of Fe, Cr, O, and other elements of the steel were observed (point 4 in Figure 8). The results confirm the formation of phases of oxides of iron and chromium on the top part of oxide node of HCM12A steel (oxide island). Moreover, some protective layers such as chromia (Cr₂O₃), mixed oxides or the mixed spinels (Fe, Cr, O, Mn) on the inner part of node (oxide crater) could be formed.

The EBSD micrograph and a line scan analysis of the cross-section of an oxide node of the HCM12A at 750 °C are

shown in Figure 9a,b. The image shows an oxide node around 50 μm of thickness (Figure 9a). Therefore, a predominant fracture or rupture of the node is observed. The fracture divides the node into two zones: the top part “oxide island” between 0 and 25 μm and the inner part “oxide crater” between 25 and 50 μm. A possible cause of the fracture of the node may be the interdiffusion of the elements of the HCM12A steel and oxygen during oxidation. The interdiffusion had maybe created holes or cracks on the sample during oxidation and the fracture finally occurred over time. The line-scan analysis of oxide node of the HCM12A steel (Figure 9b) has corroborated the interdiffusion of elements of the steel in contact with the steam oxidation environment. The concentration profile of an oxide node corroborated the same results observed by EDAX analysis on four points and the composition mapping. The composition profile of outer part of the node “oxide island” indicated a major concentration of Fe (from 15 to 75 at%), O (from 5 to 25 at%), and Cr (from 15 to 45 at%). Moreover, the inner part “oxide crater” was composed of a mixture of Fe-Cr-Mn-O; Fe (from 25 to 80 at%), O (from 25 to 45 at%), Cr (from 15 to 40 at%), and

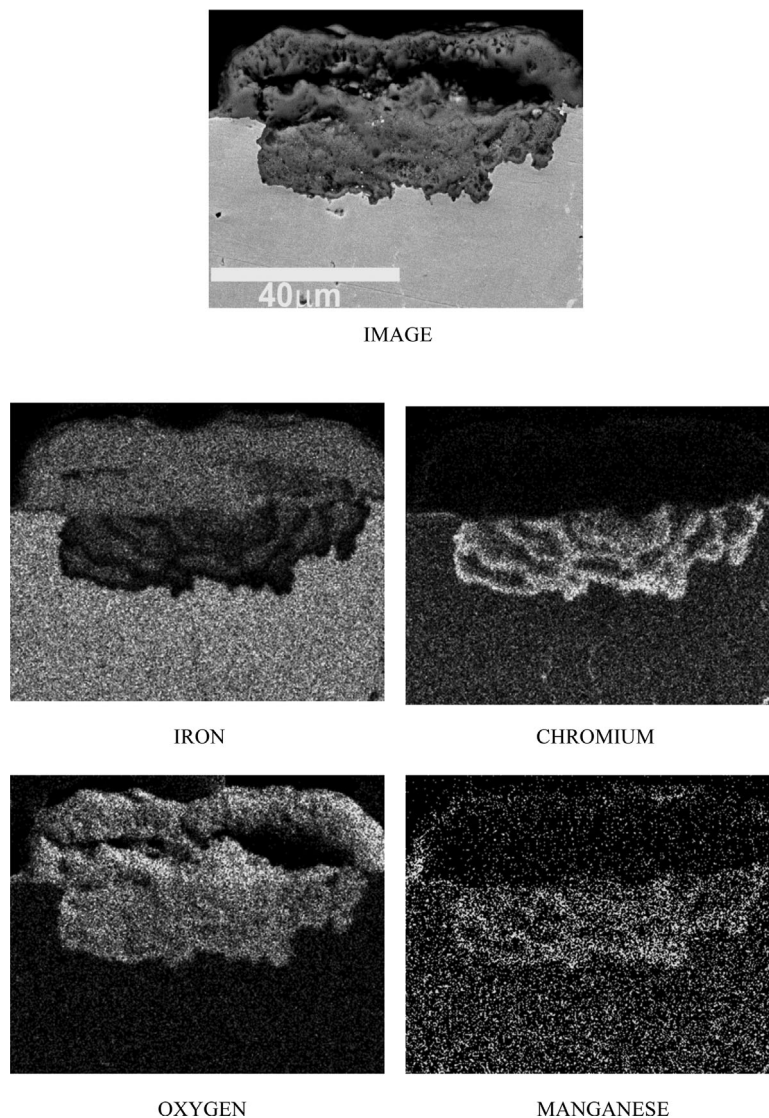


FIGURE 7 Mapping of composition of a cross section of an oxidation node of HCM12A steel at 750 °C

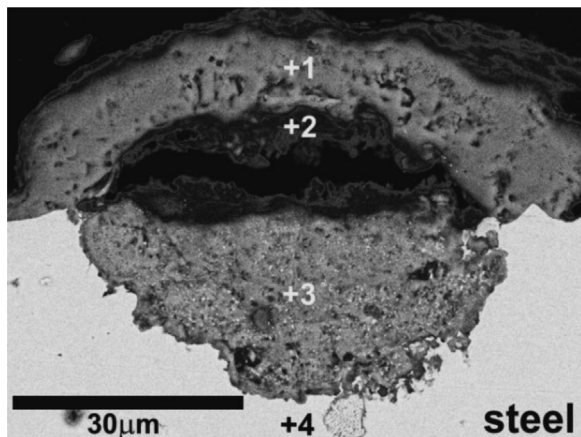


FIGURE 8 EBSD image and the EDAX analysis of small area on four points of a profile oxide node of HCM12A steel at 750 °C

Mn (from 2 to 6 at%). Places where some protective layers such as chromia (Cr_2O_3) and mixed oxides or the mixed spinels (Fe, Cr, Mn, O) could be formed. The area where the substrate comes in contact with the oxide crater, became unprotected against steam oxidation due to diffusion of chromium resulting in the formation of chromia layer. As the oxidation process continues, chromium loss and its subsequent breakdown of chromia scale are caused by volatilization. Then, Fe diffuses uncontrollably and forms with the oxygen a variety of oxides layers; such as wüstite (FeO), hematite (Fe_2O_3), and magnetite (Fe_3O_4). The oxidation catastrophe begins and eventually the phenomenon of corrosion becomes critical.

Figure 10a–c shows images generated by detection of secondary electron emission and EBSD of surface and cross section of HCM12A oxidized steel at 800 °C in Ar + 40% H_2O for 190 h. The HCM12A steel image at 800 °C (Figure 10a) shows a rough and granular surface similar to

TABLE 2 EDAX analysis on four points of a cross section of HCM12A oxidized steel at 750 °C for 190 h

Points of Figure 8	Wt%									
	Fe	Cr	O	Mn	C	V	W	Ni	Cu	Mo
(1)	58.28	1.43	33.79	0.37	6.13	–	–	–	–	–
(2)	66.20	6.47	24.98	1.42	0.94	–	–	–	–	–
(3)	32.55	24.62	32.77	0.86	3.76	0.38	4.00	0.48	0.58	–
(4)	55.06	6.28	31.54	0.26	4.51	–	1.42	0.27	0.39	0.26

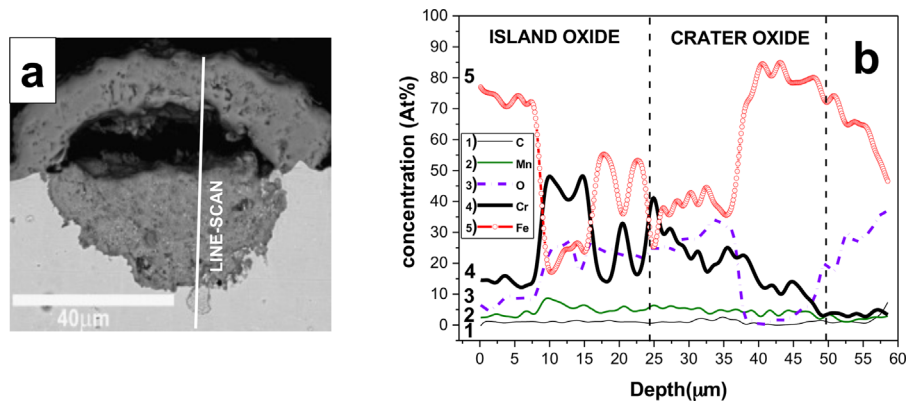


FIGURE 9 Micrograph and EDAX analysis of an oxide node of HCM12A steel at 750 °C: (a) EBSD image of cross section and (b) line-scan analysis. [Color figure can be viewed at wileyonlinelibrary.com]

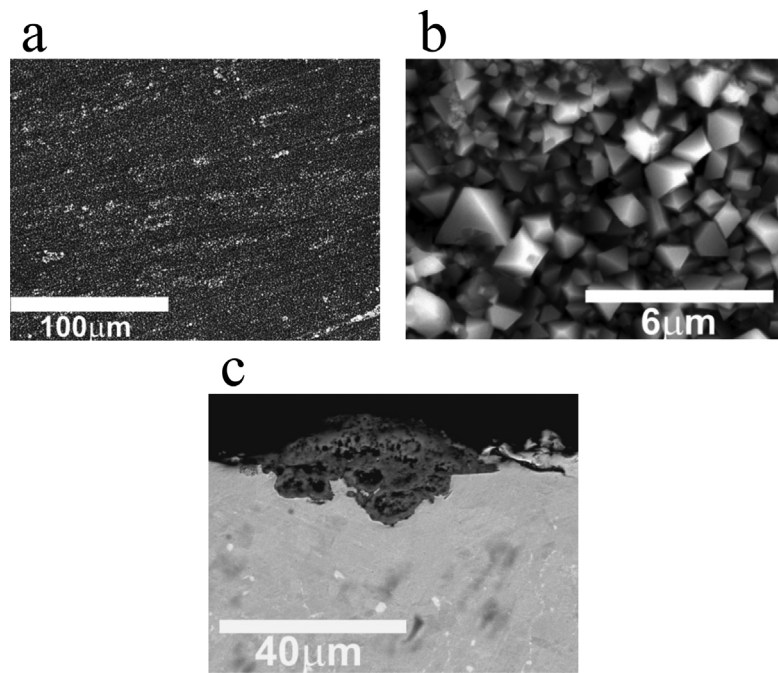


FIGURE 10 Micrographs at different magnifications of oxide scale of HCM12A steel at 800 °C in Ar + 40% H_2O for 190 h; (a,b) SEM images of surface and (c) EBSD image of a cross section of an oxide node

the oxidized HCM12A steel at 750 °C. The oxide scale surface contained many crystals of different sizes, from 0.07 to 0.25 μm (Figure 10b). Furthermore, the sample extracted from the oxidation system lost material from the oxide scale and showed few oxidation nodules. This was possible due to the micro-

tensions created by the cooling on the oxide surface of the steel after its extraction. EDAX analysis of a small area of surface of the oxide of the HCM12A steel at 800 °C (Figure 10c) confirmed the composition of Fe = 49.10, Cr = 9.81, O = 30.50, Mn = 7.54, Si = 0.30, C = 1.42, V = 0.28, and

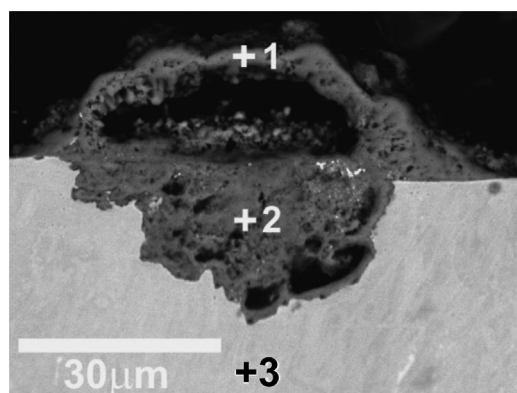


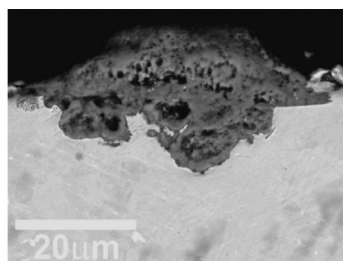
FIGURE 11 EBSD image and the EDAX analysis of small area on three points of a profile oxide node of HCM12A steel at 800 °C

Cu = 1.05 (wt%). These results suggest a predominant formation of Fe, Cr, and Mn oxide phases on the steel surface, such as Cr_2O_3 protective layers, FeCr_2O_4 mixed spinel and another possible mixed spinel (Fe, Cr, Mn, O). The EBSD micrograph at high magnification of a cross section of this oxidized steel (Figure 10c) shows a porous oxide node of 25 μm of thickness.

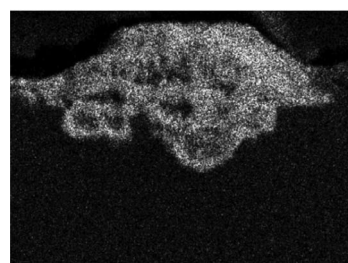
An EBSD image and the EDAX analysis of small area on three points of a cross section of an oxide node of HCM12A steel oxidized at 800 °C (Figure 11 and Table 3) once again verified high concentrations of Fe and O, and low concentrations of Cr and Mn in the top part (point 1 in Figure 11) “oxide island.” Thus, higher concentrations of Cr, O, Fe and low concentration of Mn were observed in the inner

TABLE 3 EDAX analysis on three points of a cross section of HCM12A oxidized steel at 800 °C for 190 h

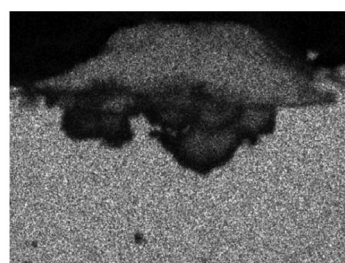
Points of Figure 11	Wt%								
	Fe	Cr	O	Mn	C	V	W	Ni	Cu
(1)	59.09	1.14	32.50	1.55	5.41	0.03	0.34	–	–
(2)	14.96	37.46	37.16	1.78	5.11	0.35	1.66	0.45	1.07
(3)	52.40	7.29	32.65	0.34	5.03	0.13	1.26	0.28	0.62



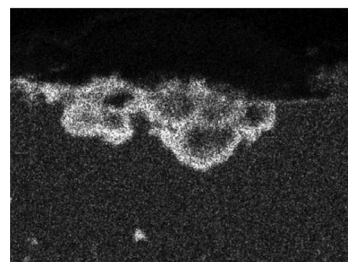
IMAGE



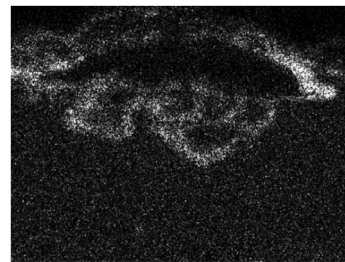
OXYGEN



IRON



CHROMIUM



MANGANESE

FIGURE 12 Mapping of composition of a cross section of an oxidation node of HCM12A steel at 800 °C

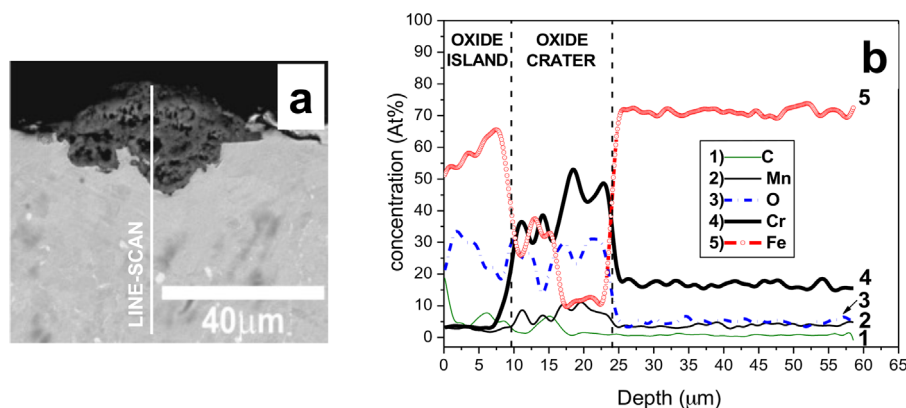


FIGURE 13 Micrograph and EDAX analysis of cross section of an oxide node of HCM12A steel at 800 °C: (a) EBSD image and (b) line-scan analysis. [Color figure can be viewed at wileyonlinelibrary.com]

part of node “oxide crater”; a possible place where protective layers such as the chromia or mixed oxides or some mixed spinel (Cr, Fe, Mn, O) were formed. Finally, the composition of the steel and the oxygen were observed on the bottom of the sample (point 3 in Figure 11).

An EBSD image and its respective mapping of the composition in a cross-section of oxide scale for HCM12A oxidized steel at 800 °C are shown in Figure 12. According to the results, oxide node size around 25 μm thick could be verified, with two zones: an “oxide island” (10 μm) and an “oxide crater” (15 μm). On the other hand, the possible cause of fracture of oxide scale on HCM12A steel oxidized in steam could be due to interdiffusion of some elements of the steel (Fe, Cr, Mn) by the oxidation environment.

Also, EBSD micrograph and the line-scan analysis of cross-section of oxide scale (Figure 13a,b) verified not only the composition of the diffused elements during oxidation but also the formation of an oxidation node of 25 μm approximately, consisting of an “oxide island” of 10 μm and an “oxide crater” of 15 μm. The highest concentrations of Fe and O in the upper part “oxide island” of the oxide node were corroborated again, where mainly iron oxides were formed. While high concentrations of Cr, Fe, O and low concentration of Mn were found in the inner part of the nodule (oxide crater); a place where protective layers such as chromia or some mixed spinel were formed. Thus, the composition of the oxide scale at different depths has verified the interdiffusion of elements to the surface of the steel (Fe, Cr, Mn), and the oxygen of the steam into the sample. Moreover, the analysis indicated that manganese diffused throughout the whole oxide scale in a constant way.

Figure 14a,b shows results from XRD analysis in (θ-2θ) angle mode of the HCM12A oxidized steel in steam at 750 and 800 °C. The diffractogram of the steel oxidized at 750 °C (Figure 14a) confirmed possible crystalline phases approximated by EDAX analysis such as hematite Fe_2O_3 ^[36]

of rhombohedral structure. Moreover, other reflections show phases belonging to the cubic structure, such as magnetite Fe_3O_4 ,^[37] the mixed oxides $(\text{Cr, Fe})_2\text{O}_3$ ^[38] and Fe ^[39] of the steel. XRD analysis of HCM12A steel oxidized at 800 °C (Figure 14b) confirmed the same crystalline phases previously observed for steel HCM12A at 750 °C. In addition, another crystalline phase known as chromia Cr_2O_3 ^[40] of rhombohedral structure was observed.

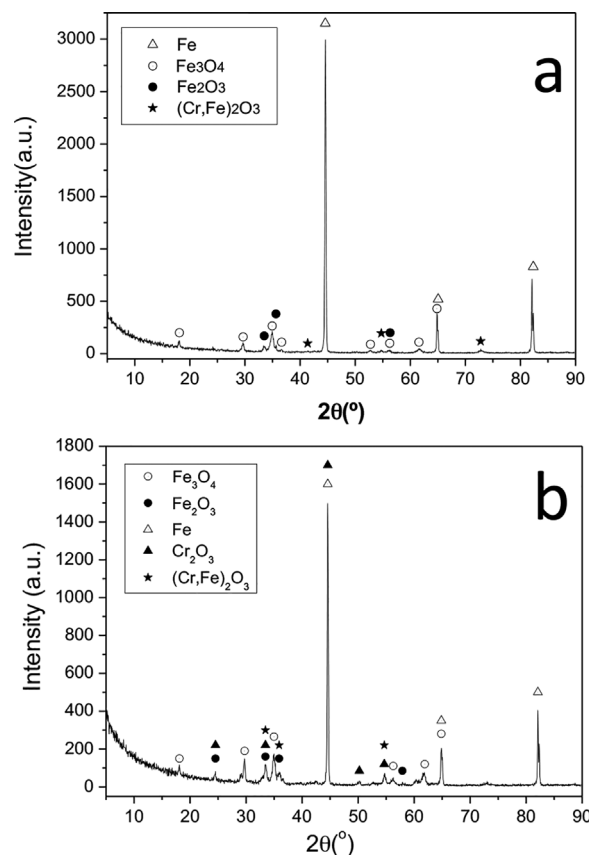


FIGURE 14 XRD patterns in (θ-2θ) angle mode taken for the HCM12A steels oxidized in steam at two oxidation temperatures: (a) 750 °C and (b) 800 °C

All these results corroborate the better performance of the HCM12 oxidized steel under these critical steam oxidation conditions. The protective layers formed on the HCM12A steel during oxidation are very important because they help prevent or retard oxidation catastrophe of steel. In addition, these results corroborated a better performance of HCM12A steel compared to other oxidized ferritic/martensitic steels (P91, P92, FB2A) under the same oxidation conditions.^[20,21,34,35]

4 | CONCLUSIONS

The oxidation behavior of the ferritic/martensitic HCM12A steel at 750 and 800 °C in Ar + 40% H₂O steam for 190 h was researched. Theoretical equilibrium simulations using the Thermo-calc program for a 500–900 °C oxidation temperature range have contributed significantly and they reported on the formation of some solid phases such as the mixed spinel Cr₂FeO₄, the oxide FeO (wüstite), the mixed oxides FeWO₄ and MnWO₄, and the alloy BCC-A2 phase of Fe_{0.7098}Cr_{0.2049}W_{0.0022}Mn_{0.0017}Mo_{0.0015}. These phases were calculated with a high probability of formation on the steel. The high negativity of total Gibbs free energy calculated of the oxidation system ($\Delta G \sim -16348$ kJ/mol) has guaranteed a high thermodynamic probability of formation of the solid phases aforementioned. In addition, some gaseous species (in the form of oxides, hydroxides, and oxyhydroxides of Fe, Cr, Ni, Mn, and Mo) were also calculated at this temperature range.

The experimental results of HCM12A oxidized sample verified the formation of protective layers such as hematite (Fe₂O₃), magnetite (Fe₃O₄), and chromia (Cr₂O₃) and the mixed oxides ((Cr, Fe)₂O₃). Moreover, Fe of the steel was observed. MS analysis during different oxidation times of HCM12A steel corroborated the good behavior of steel against steam oxidation. Volatile species of hydroxides Mn(OH)₃(g) and Mn(OH)₇(g), and the oxyhydroxide CrOOH(g) of small intensity (between 1 and 3 ppm) were observed during steam oxidation of HCM12A steel at 750 °C, where Mn(OH)₃(g) was the predominant volatile species. Whereas, only a predominant common species of chromium i.e., CrOOH (g) of major intensity (between 5 and 6 ppm) was observed throughout the test at 800 °C of this steel. The protective layers reduced loss of chromium and delayed the catastrophic oxidation of the steel.

The thermogravimetric measurements confirmed once again the best performance of HCM12 oxidized steel under these critical steam oxidation conditions. The oxidized HCM12A steel at 750 °C gained a small amount of mass around 0.11375 mg/cm², while the same oxidized steel at 800 °C gained almost double of mass. Moreover, by TAG, MS, SEM, EBSD, EDAX, and XRD results, we have verified that the HCM12A steel has better performance against steam

oxidation at high temperature in comparison with other ferritic/martensitic steels (P91, P92, FB2A)^[21,34,35]; for example, the P91 steel oxidized at 650 °C under similar conditions^[21] has reported a mass gain up to 80 times in comparison to mass gain of HCM12A steel oxidized at 800 °C.

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