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Comparative Study of High Temperature Oxidation Behaviour in AISI 304 and AISI 439 Stainless Steels

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This work deals with a comparison of high temperature oxidation behaviour in AISI 304 austenitic and AISI 439 ferritic stainless steels. The oxidation experiments were performed between 850 and 950 °C, in oxygen and Ar (100 vpm H_2). In most cases, it was formed a Cr_2O_3 protective scale, whose growth kinetics follows a parabolic law. The exception was for the the AISI 304 steel, at 950 °C, in oxygen atmosphere, which forms an iron oxide external layer. The oxidation resistance of the AISI 439 does not depend on the atmosphere. The AISI 304 has the same oxidation resistance in both atmospheres, at 850 °C, but at higher temperatures, its oxidation rate strongly increases in oxygen atmosphere. Concerning the performance of these steels under oxidation, our results show that the AISI 439 steel has higher oxidation resistance in oxidizing atmosphere, above 850 °C, while, in low pO_2 atmosphere, the AISI 304 steel has higher oxidation resistance than the AISI 439, in all the temperature range investigated.

Keywords: *oxidation, corrosion, AISI 304 stainless steel, AISI 439 stainless steel*

1. Introduction

Chromia protective films which grow on stainless steels are very effective to reduce high temperature corrosion[1,2]. Among various applications, stainless steels are today widely used in exhaust line systems to improve the service life of automotive exhaust components, specially the upstream part of the exhaust line (manifold, down-pipe, converter shell), where temperatures can reach 1100 °C.

Austenitic stainless steels like AISI 304 are traditionally used, but, recently, ferritic stainless steels have been developed for those applications. Besides offering advantage of lower costs than austenitic grades, due to the absence of nickel, they also present lower expansion coefficient than austenitic steels, which is a great advantage when temperature cycling resistance is needed.

In this work, the high temperature oxidation behaviour of an austenitic stainless steel type AISI 304 is compared to the behaviour of a 17% Cr ferritic stainless steel (AISI 439) containing titanium and niobium (see Table 1). These elements are generally added to stainless steels to prevent the risks of intergranular corrosion of weldments, due to the formation of stable titanium and niobium nitrides and carbides instead of non stable chromium carbides[3,4].

Moreover due to additions of nitride and carbide forming elements, the structure of the stabilized 17% Cr steels is "fully" ferritic at all temperatures. This property has a beneficial effect on the oxidation resistance of those steels, due to the absence of any ferrite to austenite phase transformation[5], which could damage the protective oxide film.

2. Experimental

The samples of AISI 304 austenitic and AISI 439 ferritic stainless steels used in this work were supplied by Acesita S.A. The chemical analysis of these steels are given in Table 1.

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For the thermogravimetric analyses, the samples were cut with dimensions of 10 mm × 10 mm × 0.6 mm. A small hole of 0.8 mm in diameter was drilled near an edge in order to hang the sample in the thermobalance.

The samples were polished with diamond paste, and submitted to oxidation treatments in a thermobalance SETARAM TGDTA 92, with sensibility of ±1 µg.

The oxidation treatments were performed from 850 to 950 °C, either in oxygen or in Ar-H_2 (100 vpm H_2) atmospheres. The such obtained Ar-H_2–H_2O mixture goes through a cryostat at -60 °C which maintains an H_2O pressure at 5.26×10^{-6} atm. Then, the H_2/H_2O equilibrium leads to low oxygen pressures equal to 1.46×10^{-20} atm at 850 °C, 1.38×10^{-19} atm at 900 °C, and 1.15×10^{-18} atm at 950 °C. Oxidation treatments in air were not performed as it was observed that the oxygen pressure associated to air did not induce any change in the oxidation behaviour when compared to what occurs in 1 atm oxygen. Indeed, an oxygen pressure of 0.21 atm is sufficient to allow the formation of iron oxides.

The isothermal oxidation treatments were performed for 50 h. The growth kinetics of the scales formed on the steels were established by measuring the mass gain per unit area versus oxidation time.

The microstructure and composition of the oxidized surface were examined by scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDX).

3. Results

3.1 Kinetics

Figure 1 shows the thermogravimetric analysis of the AISI 439 stainless steel during oxidation at 950 °C, in oxygen atmosphere, for 50 h. The plot of mass gain per unit area (ΔM/S) against the oxidation time (t) shown in Fig. 1 is typical for the steels studied in this work, except for the AISI 304 steel, above 850 °C, in oxygen atmosphere.

Figure 2 shows the plot of $(\Delta M/S)^2$ versus t corresponding to the thermogravimetric analysis shown in Fig. 1. In most cases, there was a linear relationship between $(\Delta M/S)^2$ and t, as shown in Fig. 2, indicating that the kinetics follow a parabolic law, according to the equation $(\Delta M/S)^2 = k_p t$. Such a parabolic law traduces the fact that the oxide growth is controlled by diffusion[6]. The k_p values are reported in Table 2. The obtained k_p values are representative of Cr_2O_3 growth[6,7].

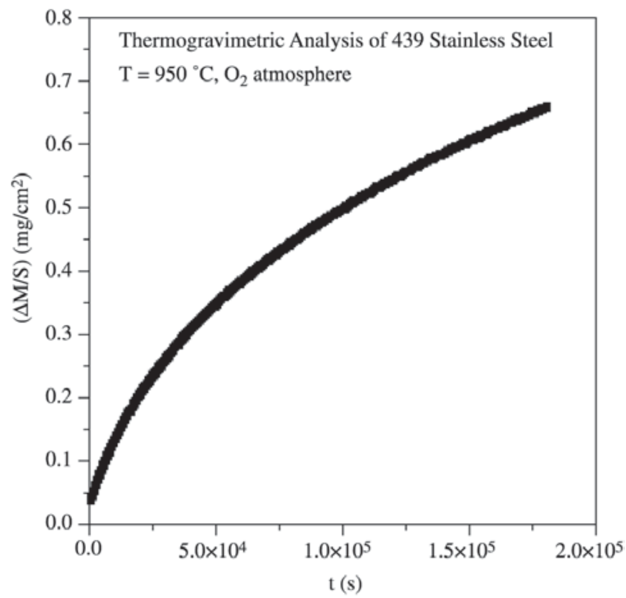


Figure 1. Evolution of the mass gain as a function of time for the 439 steel oxidized at 950 °C in oxygen.

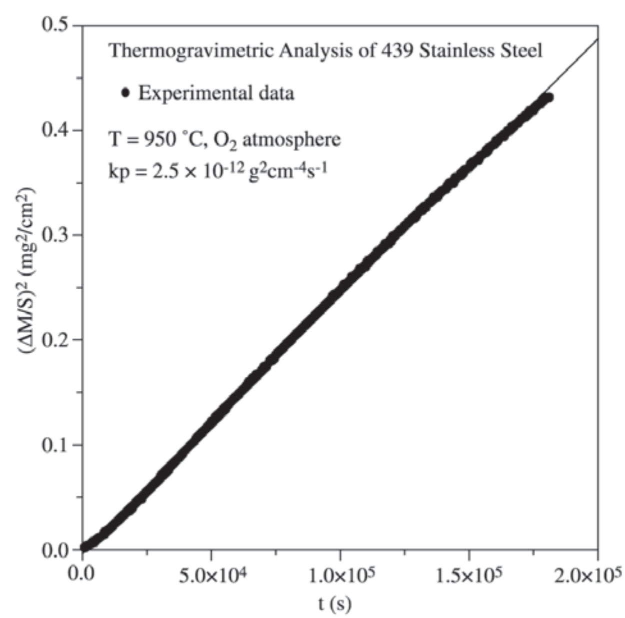


Figure 2. Quadratic plot of Fig. 1 showing that the oxidation kinetics obeys a parabolic law.

Table 1. Chemical Composition of the 304 and 439 Stainless Steels.

Steel	C (%)	Mn (%)	Si (%)	P (%)	S (%)	Cr (%)	Ni (%)	Nb (%)	Ti (%)	N (ppm)
304	0.0466	1.37	0.46	0.028	0.0006	18.07	8.11	-	-	322
439	0.0060	0.18	0.42	0.033	0.0010	17.01	0.23	0.17	0.15	122

Figure 3 shows the linearity deviation in a plot of $(\Delta M/S)^2$ versus t for the AISI 304 steel oxidized at 950 °C, in oxygen atmosphere. In this case, initially, there is formation of Cr_2O_3 scale (k_{p1} value in Table 2) followed by the formation of an iron oxide scale, little adherent, which results in high oxidation rate (k_{p2} value in Table 2). Such behavior is not found when the samples are oxidized in $Ar\text{-}H_2\text{-}H_2O$.

3.2 Oxide morphology

Concerning the 439 stainless steel, the oxide scale is always made of chromia in the temperature range or the oxidation atmosphere investigated, with some titanium and manganese oxides. This is shown by Fig. 4, which corresponds to EDX analysis on the outer surface of the scale formed at 950 °C in oxygen. The same behavior is observed at lower temperatures. When oxidized in $Ar\text{-}H_2\text{-}H_2O$, some spallings appear at 950 °C, and at the bottom of the spalled zone, oxide crystallites made of Si and Ti are detected (Fig. 5). For oxidation in $Ar\text{-}H_2\text{–}H_2O$ but at 900 °C or 850 °C, some whiskers are detected, as shown by Fig. 6.

The situation differs for 304 steel. In $Ar\text{-}H_2\text{–}H_2O$ atmosphere, the scale is made of chromia but, specially at 850 and 900 °C, extrusions are observed all along the substrate grain-boundaries (Fig. 7a), and these extrusions are made mainly of whiskers (Fig. 7b) rich in Cr and Mn.

On transverse sections, it is possible to observe silica at the metal-oxide interface, under the chromia layer (Fig. 8). When the 304 steel is oxidised in O_2, the scale is made of chromia plus Mn oxide at 850 and 900 °C, but at 950 °C, the scale is made of an outer layer of iron oxide (Fig. 9a) whose aspect differs of the aspect given by the chromia layer which is observed when spalling of the outer layer occurs (Fig. 9b).

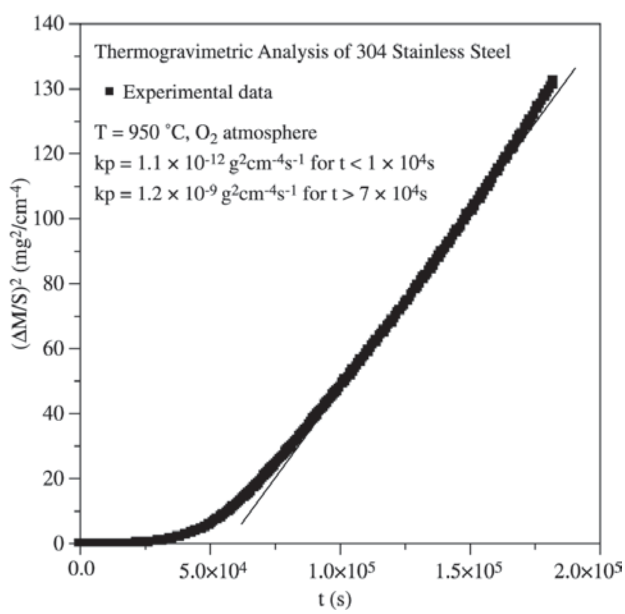


Figure 3. Quadratic plot of the mass gain versus time for the 304 steel oxidized at 950 °C in oxygen, showing two oxidation stages, a slow first one and a second much more fast.

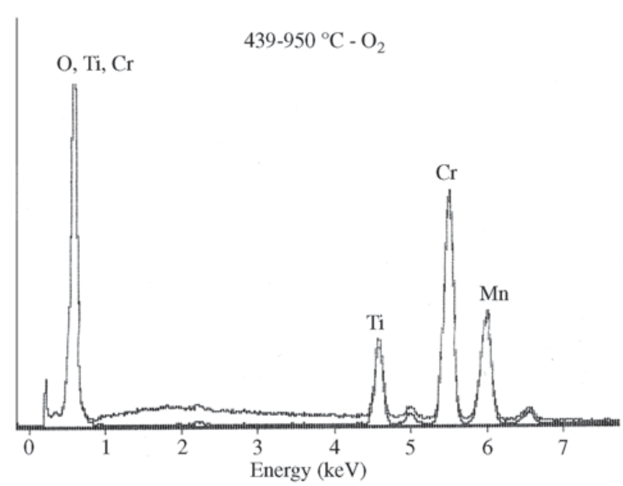


Figure 4. EDX analysis on the surface of the 439 steel oxidized at 950 °C in oxygen showing that the oxide scale contains Cr, Ti and Mn.

Table 2. Parabolic oxidation constants.

	439 Stainless steel		304 Stainless steel	
Atmosphere→	O_2	$Ar\text{-}H_2$	O_2	$Ar\text{-}H_2$
Temperature (°C)¯	k_p ($g^2cm^{-4}s^{-1}$)	k_p ($g^2cm^{-4}s^{-1}$)	k_p ($g^2cm^{-4}s^{-1}$)	k_p ($g^2cm^{-4}s^{-1}$)
850	3.2×10^{-13}	2.9×10^{-13}	1.3×10^{-13}	1.6×10^{-13}
900	1.4×10^{-12}	1.5×10^{-12}	6.2×10^{-12}	3.0×10^{-13}
950	2.5×10^{-12}	2.6×10^{-12}	$t<10^4$s : 1.1×10^{-12} (kp_1) $t>7\times10^4$s : 1.2×10^{-9} (kp_2)	6.4×10^{-13}

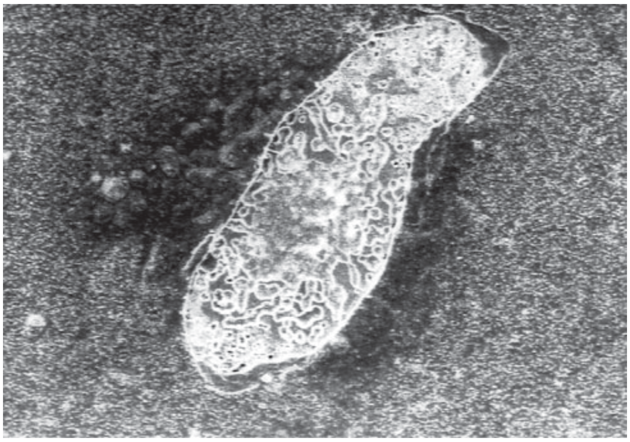


Figure 5. Observation of a spalled zone by SEM on the 439 steel oxidized at 950 °C in Ar-H_2-H_2O for 50 h (275×).

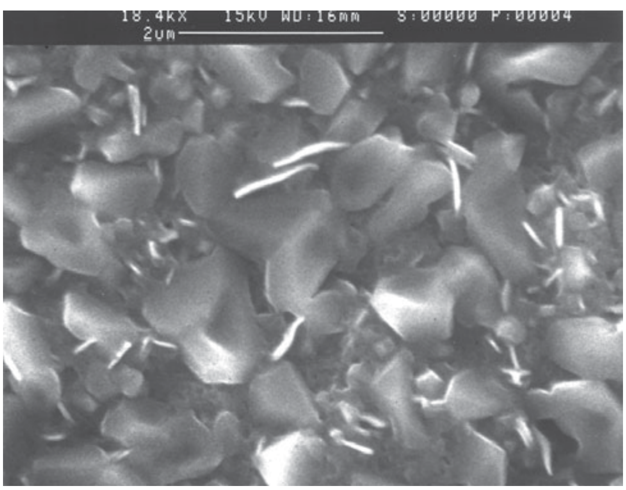
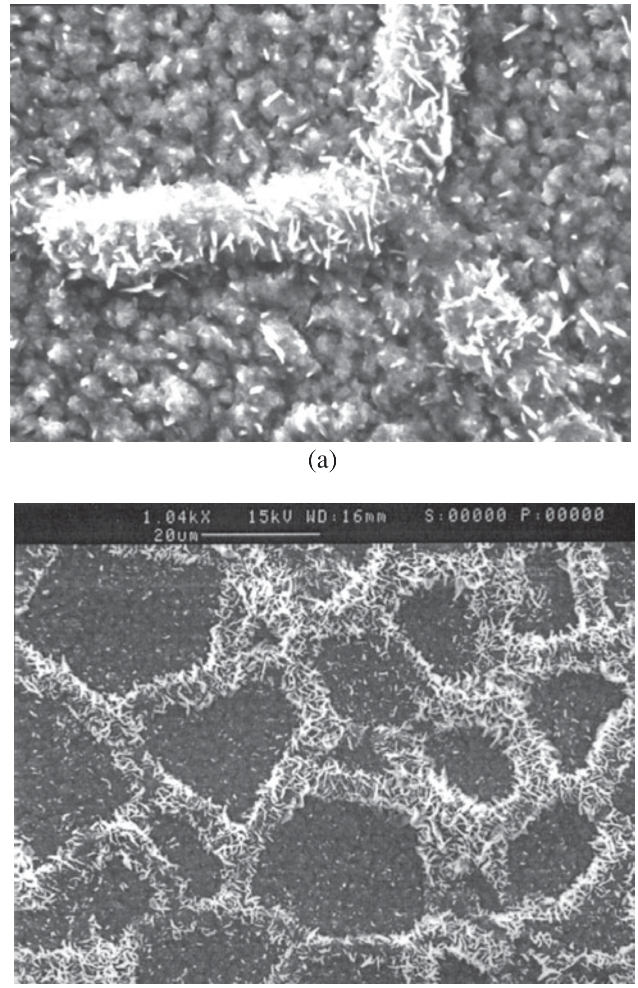


Figure 6. Observation of the surface of the oxidized 439 steel after 50h at 850 °C in Ar-H_2-H_2O mixture (18400×).



(a)

(b)

Figure 7. Observation of the surface of oxidized 304 steel. a) in Ar-H_2-H_2O at 850 °C (4470×); b) in Ar-H_2-H_2O at 900 °C (1040×).

4. Discussion

Figure 10 shows a comparison of the oxidation rates of the AISI 439 steel in low pO_2 atmosphere and in oxidizing atmospheres. For this steel, the oxidation rate has no significant dependence on both atmospheres used. In all cases, chromium oxide is formed. In Ar-H_2-H_2O mixture, iron oxides are thermodynamically unstable while Cr_2O_3 is stable[2], consequently only this chromium oxide can grow. In oxygen atmosphere, all oxides (iron and chromium oxides) are thermodynamically stable and the scale growth is then controlled by kinetic factors. Cr_2O_3 is always the most stable oxide, but its growth as a continuous film will be possible if the chromium amount is higher than a critical value given by[6]:

$$N_{Cr}^{Min} = F\left[\left(\frac{1}{2}\frac{k_c(Cr_2O_3)}{\tilde{D}}\right)^{1/2}\right] \quad (1)$$

where

$$F(u) = p^{1/2}u(1\text{-erf } u)\exp(u^2)$$

with

$$\text{erf } u = \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}\,du$$

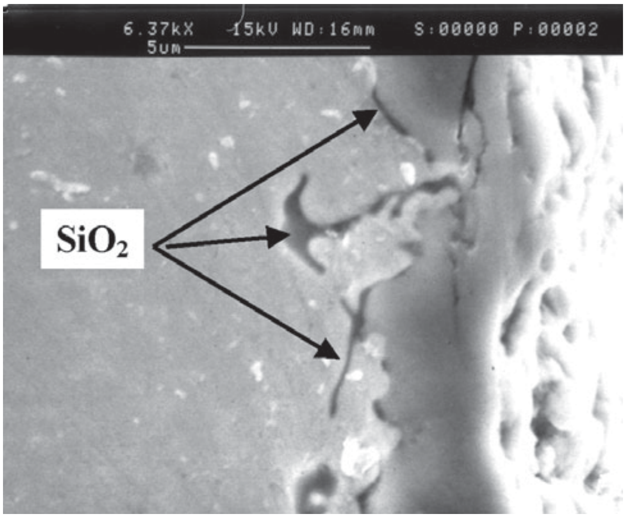


Figure 8. Transverse section showing the inner chromia scale with silica at the bottom (dark zones). Oxidation of 304 steel for 50 h at 950 °C in O_2.

k_c (Cr_2O_3) is the parabolic oxidation constant of chromia expressed in cm^2/s, and $\tilde{D}$ is the interdiffusion coefficient in the metallic substrate.

For an oxide M_aO_b, k_c is related to k_p (Table 2) by:

$$k_c = \left(\frac{M_{ox}}{b\rho_{ox}M_o}\right)k_p \qquad (2)$$

where the subscript "ox" and "o" are relative to the oxide and the oxygen species, respectively, M is the molar mass and ρ the volumetric mass.

Moulin[8] gives a value of N_{Cr}^{Min} around 0.15 at 900 °C. Thus the chromium amount in the 439 steel is higher than this value and a chromia layer can form, as soon as the oxidation begins, as a continuous layer. In such conditions, iron oxides do not grow. Moreover the activation energy of oxidation, calculated from the slope of the curves in Fig. 10, is equal to ≈ 250 kJ/mol, which is a value given in the literature for some chromia film growth[9,10].

The plot of Fig. 11 shows the influence of the atmosphere on the oxidation rate of the AISI 304 steel. At 850 °C, there is no significative effect of the atmosphere, due to the formation of Cr_2O_3 in both cases. However, at higher temperatures, the oxidation rate of this steel, in oxygen atmopshere, is much greater than in Ar-H_2–H_2O atmosphere on account of formation of iron oxide. For oxygen pressures imposed by the Ar-H_2–H_2O mixture, iron oxides are thermodynamically unstable[2], while chromia is stable. Thus, only this oxide appears in Ar-H_2–H_2O. When the oxygen pressure is sufficient to form chromium and iron oxides, i.e., in 1 atm oxygen, the diffusion coefficients in the austenitic substrate being smaller than in the previous case (D in ferritic steel is fairly 10 times higher than in an austenitic steel), the minimum content of chromium, given by Eq. 1, can become higher than the chromium amount in the 304 steel. This seems to be the case, at least at 950 °C, and iron oxides appear simultaneously to chromia. It can be noted that the activation energy of chromia growth (see Table 3) for 304 steel in Ar-H_2–H_2O equal to 156 kJ/mol (Figs. 11 and 13), as found by some authors[11,12], is smaller than the activation energy for chromia growth on the 439 steel whose activation energy associated to chromia growth is about 240 $kJ.mol^{-1}$ (Table 3 and Figs. 10, 12 and 13). Perhaps

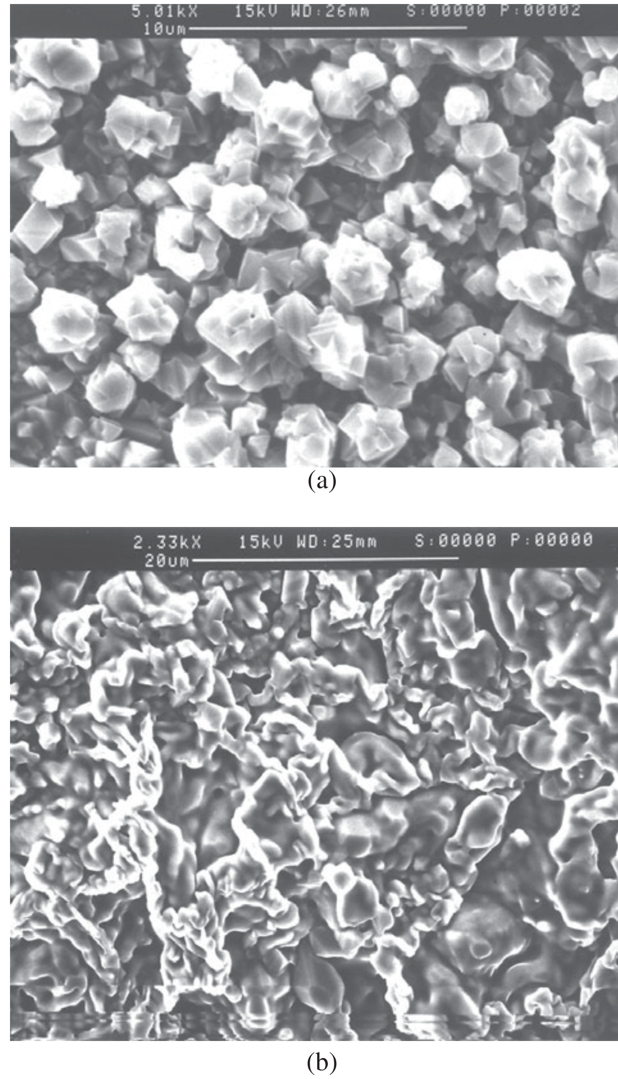


Figure 9. Observation of the surface of the 304 steel oxidized in oxygen at 950 °C: a) bottom of a spalled zone: chromium oxide; b) unspalled surface, iron oxide.

Table 3. Activation energies for oxidation.

Atmosphere	Activation Energy (kJ/mol) 304 Steel	439 Steel
O_2	"1052"*	237
$Ar-H_2-H_2O$	156	251

* this value is not significant as the oxide formed differs at low an high temperature.

this difference is associated to manganese which is more present in 304 steel and which is a very oxidizable element (more oxidizable than chromium). Simultaneously to the difference in the activation energy, the oxidation rate of 304 steel in $Ar-H_2-H_2O$ is smaller than the oxidation rate of 439 steel, in all temperature range investigated as shown by

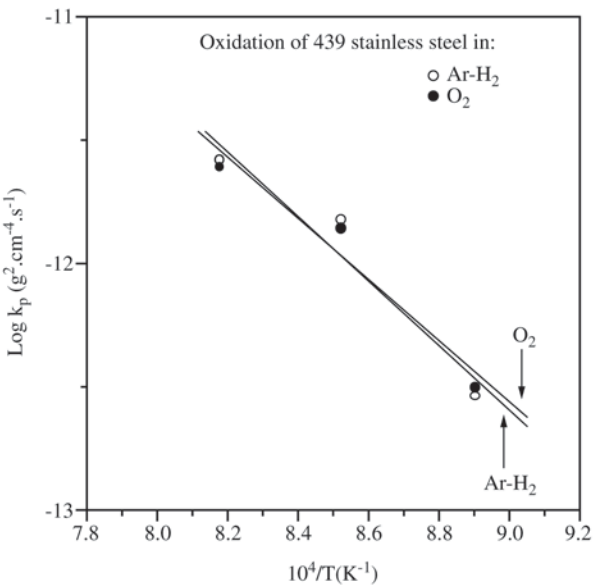


Figure 10. Arrhenius plot of the parabolic oxidation constants of 439 steel in oxygen and in $Ar-H_2-H_2O$ atmospheres.

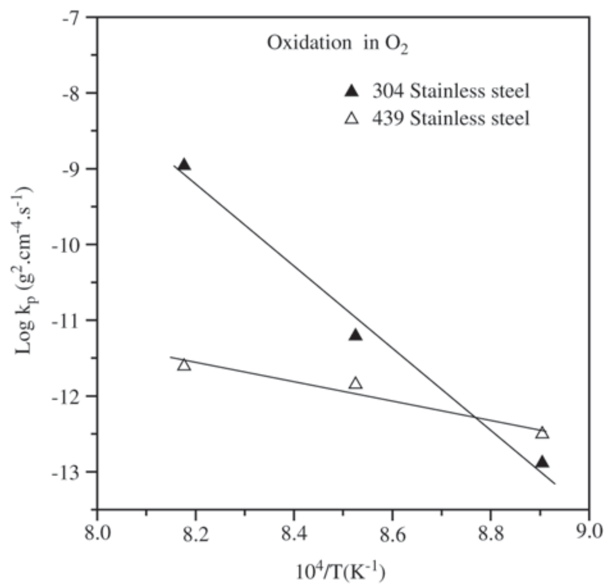


Figure 12. Arrhenius plot of the parabolic oxidation constants of 304 and 439 steels in oxygen.

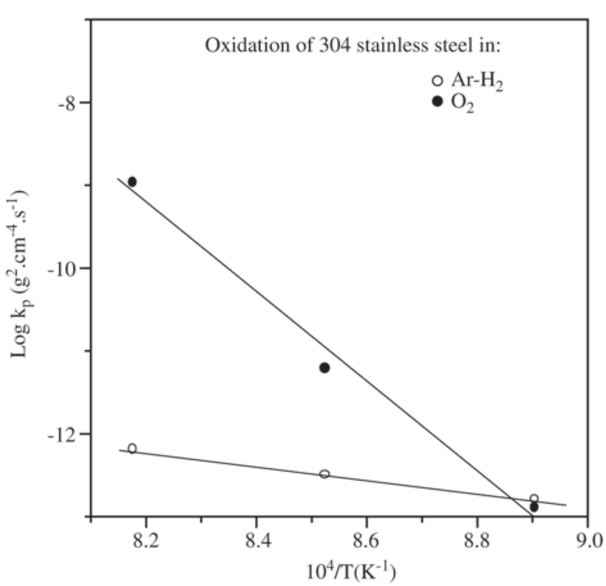


Figure 11. Arrhenius plot of the parabolic oxidation constants of 304 steel in oxygen and in $Ar-H_2-H_2O$ atmospheres.

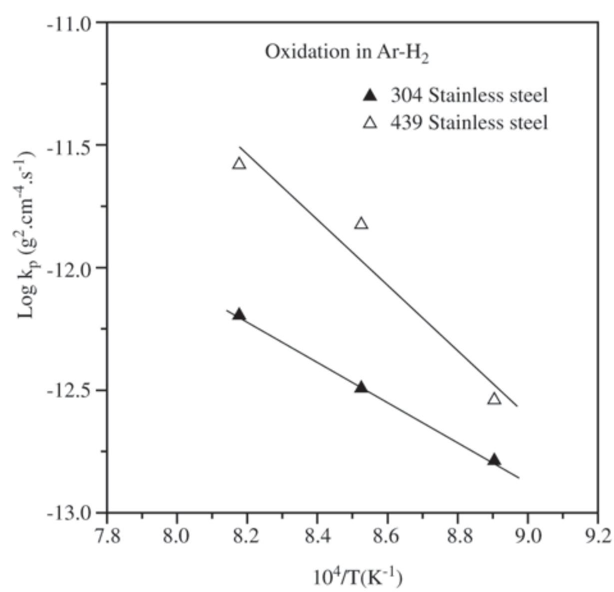


Figure 13. Arrhenius plot of the parabolic oxidation constants of 304 and 439 steels in $Ar-H_2-H_2O$.

Fig. 13. This suggests that oxidation of Mn reduces iron oxidation and incorporation in the chromia scale. In other words, the presence of Mn seems to promote the formation of a continuous chromia scale. Nevertheless, an effect of the oxygen pressure decrease on the chromia growth rate cannot be excluded[13].

The plots of Figs. 12 and 13 are a comparison of the oxidation behaviour of the AISI 304 and AISI 439 steels, between 850 and 950 °C, in oxygen and in Ar-H_2-H_2O atmosphere, respectively. In oxygen, it is clear that above 850 °C, the AISI 304 steel has less oxidation resistance than the AISI 439 steel. Again, this is related to the fact that, at 950 °C, a protective chromia layer is formed only on the 439 ferritic steel. The growth of iron oxides on the 304 steel must already begin at 900 °C. In Ar-H_2, Fig. 13 clearly shows that the austenitic AISI 304 steel has higher oxidation resistance than the ferritic AISI 439 steel in low pO_2 atmosphere. Perhaps it is related to the presence of Nb and Ti in the 439 steel which can promote spallings (see Fig.5). The spallings induce fast re-oxidation of the bare substrate. Moreover, in the temperature range from 850 to 950 °C, the AISI 304 steel forms an homogeneous scale of Cr_2O_3, in which grain-boundaries of the substrate are decorated by whiskers of Cr oxide containing Mn. Mn seems to have rather a favourable effect.

5. Conclusions

- A comparative study of high temperature oxidation behaviour in AISI 304 and AISI 439 stainless steels was performed between 850 and 950 °C, in oxygen and Ar-H_2–H_2O (100 vpm H_2) atmospheres.
- Concerning the effect of the atmosphere on oxidation behaviour of each steel, our results show that: The oxidation resistance of the AISI 439 does not depend on the atmosphere. On the other hand, the AISI 304 steel has the same oxidation behaviour in both atmospheres, at 850 °C, but, at higher temperatures, its oxidation rate dramatically increases in oxygen atmosphere, in comparison to that observed in Ar-H_2-H_2O atmosphere.
- Concerning the performance of the steels under oxidation, our results show that: The AISI 439 steel has higher oxidation resistance than the AISI 304, in oxidizing atmosphere, for temperatures above 850 °C, while the AISI 304 steel has higher oxidation resistance than the AISI 439, in low pO_2 atmosphere, in all the temperature range investigated.
- In most cases, a Cr_2O_3 protective scale was formed, whose growth kinetics follows a parabolic law. The exception was for the AISI 304 steel, at 950 °C, in oxygen atmosphere, which forms an iron oxide external scale, non-adherent, which results in a higher oxidation rate.

Acknowledgments

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