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Oxidation of stainless steels (AISI 304 and 316) at high temperature. Influence on the metallic substratum

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Abstract. — Stainless steels of type AISI 304 and 316 were heated in air (1-5-15 minutes at 900-1000-1100 °C) and the oxide layers formed on the surface were analyzed by XRD, CEMS, SIMS and FTIR. At these temperatures the main oxides are Cr_2O_3 and a spinel close to MnCr_2O_4 for polishing samples (with Fe_2O_3 for the chemically cleaned samples). The oxidation induces a Cr and Mn depletion from the metallic substratum and a phase transformation γ (f.c.c.) \rightarrow α (b.c.c.) in a thin layer of the steels near the oxides – metal interface.

1. Introduction.

Stainless steels are known to exhibit corrosion and oxidation resisting qualities. In this group of alloys AISI 304 and 316 are widely used. They contain about 18 pct of chromium and 10 pct of nickel and are austenitic steels.

This paper presents an experimental study of the high temperature oxidation of these alloys, characterizes the oxide layer formed and reveals the chemical and structural modifications of the contiguous metallic phase.

2. Experimental procedure.

The samples were cut into 10 mm \times 10 mm squares of commercially-produced steel-sheets with a thickness of 0.91 mm. AISI 316 stainless steel contains 3 wt% Mo in addition to similar constituents of AISI 304 stainless steel (Cr 16.5-20, Ni 8-14, Mn \leq 2, Si \leq 1, all in weight per cent). They were either mechanically polished (3 μm grad diamond paste) or chemically cleaned (HCl/HNO₃ mixture) rinsed in ethanol and dried.

After these treatments the samples were thermally oxidized in air at different temperatures (900 °C - 1000 °C - 1100 °C) during different periods of time (1-5-15 min) and rapidly cooled in air to room temperature.

Samples were examined by conversion electron Mössbauer spectrometry (C.E.M.S.). Standard computer fitting routines were used to fit the Mössbauer spectra and obtain the isomer shift (I.S.), quadrupole splitting (Q.S.), internal magnetic field (H). Comparison with known parameters led to the identification of Fe-containing phases.

X-ray diffraction (XRD) scans were made using two different equipments: Either a classical Bragg Brentano diffractometer using $\text{CoK}\alpha$ radiation (Fe filter) or a near grazing incidence equipment with a curved sensitive detector (INEL) using $\text{CoK}\alpha_1$ radiation.

Depth profiles of some polished samples were obtained by dynamic SIMS. Spectra were acquired with a 20 keV Ga^+ source using a beam current of 6 nA in areas of $40 \times 40 \mu\text{m}^2$ removing about 2.5 nm s^{-1} . Ions were separated by a quadrupole mass filter and detected by a channeltron.

Reflectance infrared spectra were recorded with a Fourier transform spectrophotometer 710 Nicolet ($6000\text{-}250 \text{ cm}^{-1}$) equipped with reflectance attachment. The angles of incidence were 16° or 80° . The incident beam was unpolarized.

3. Results.

3.1 CHARACTERISATION OF THE SURFACE OXIDE FORMED. — The XRD spectra show the presence of $\alpha\text{Fe}_2\text{O}_3$, Cr_2O_3 and a spinel oxide. The composition of oxide layers depends on the surface preparation. The spinel oxide is always present. Although a small lattice parameter variation is observed (0.845-0.847 nm), it is close to that of MnFe_2O_4 and appreciably different from that of Ni-Cr-Fe spinel oxides (Tab. I).

Table I. — *Lattice parameters for Ni-Fe-Mn-Cr spinel oxides.*

Spinel	Lattice parameter (nm)		Ref	Spinel	Lattice parameter (nm)		Ref
Fe_3O_4	0.8397	0.8396	[1, 2]	$\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$	0.8378		[5]
FeCr_2O_4	0.8357	0.8377	[1, 4]	NiFe_2O_4	0.8399		[2]
MnFe_2O_4	0.8507		[4]	$\text{NiFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$	0.8316	0.8320	[5, 1]
MnCr_2O_4	0.8487	0.8437	[1, 3]	NiFeCrO_4	0.8324	0.8305	[5, 1]
NiCr_2O_4	0.8316		[2]	$\text{NiFe}_{0.5}\text{Cr}_{1.5}\text{O}_4$	0.8317	0.8310	[5, 1]

For the polished samples Cr_2O_3 and a spinel oxide are the main phases of the oxide layers; Fe_2O_3 is not observed for oxidation at 1100°C up to 15 minutes. For the chemically cleaned samples $\alpha\text{Fe}_2\text{O}_3$ appears immediately in the oxidation process and remains the main phase with Cr_2O_3 and the spinel oxide (Fig. 1).

The CEMS results of the chemically cleaned samples confirm the presence of $\alpha\text{Fe}_2\text{O}_3$ with the magnetically split spectrum (I.S. = 0.35 mm s^{-1} ; Q.S. = 0.2 mm s^{-1} , $\bar{H} = 520 \text{ kOe}$) and show a very weak spectrum which can be attributed to Fe_3O_4 or a non stoichiometric magnetite (I.S. : 0.23 mm s^{-1} and 0.71 mm s^{-1} , $\bar{H} = 480$ and 460 kOe).

It is different for the polished samples, which present a paramagnetic doublet (I.S. = 0.36 mm s^{-1} , Q.S. = 0.44 mm s^{-1}) corresponding to the superparamagnetism of fine iron oxide.

No evidence was found for the presence of a spinel phase close to MnFe_2O_4 in the CEMS data.

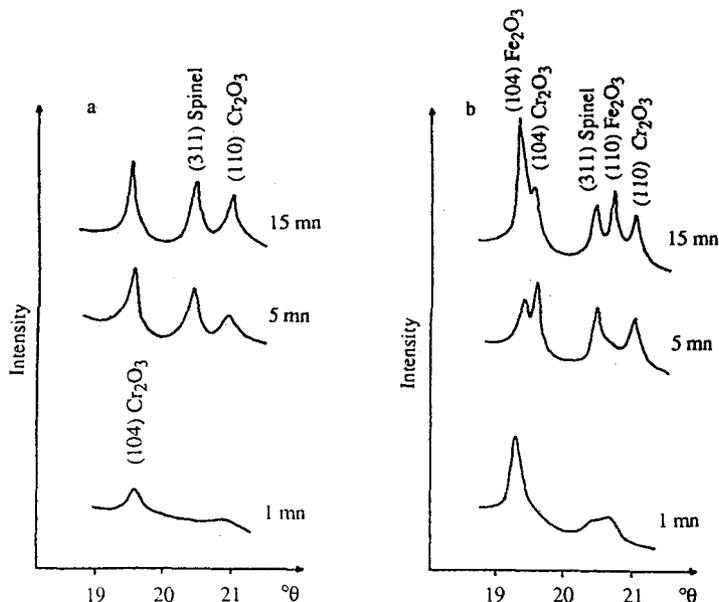


Fig. 1. — XRD spectra of AISI 304 oxidized at 1100 °C 1-5-15 mn: a) polished; b) chemically cleaned.

In figure 2 a SIMS depth profile is shown in which the enrichment of manganese and chromium is clearly visible at the outer surface. This leads to identify the spinel phase as MnCr_2O_4 . In the inner layer the relative intensity of the Cr^+ ions grows and can indicate a mixture of Cr_2O_3 and manganese chromite. The other oxidized elements are near the oxides-metal interface.

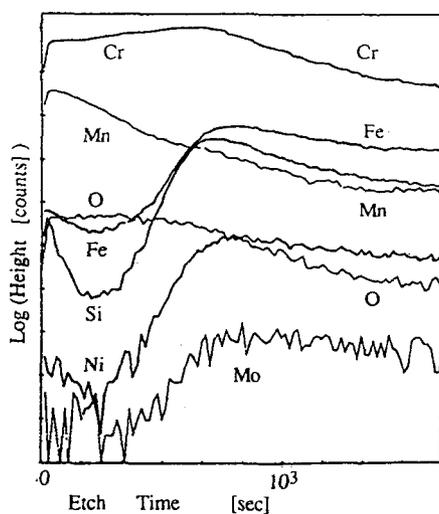


Fig. 2. — SIMS depth profiles of AISI 316 oxidized 15 mn at 1000 °C (polished sample).

It is interesting to see the manganese enrichment of oxide layers which is not indicated by other authors who study the same stainless steels heated below 900 °C [6].

The feasibility of employing reflectance infrared spectroscopy to analyse the composition, thickness and growth of thin films on metal surfaces has been discussed and demonstrated by several investigators. The fingerprinting identification procedure implies the preliminary study of reference compounds synthesized on the appropriate substrate (Tab. II).

Table II. — Analysis of infrared reflectance spectra of oxide layers on metal.

REFLECTANCE SPECTRA	System		Band positions (cm ⁻¹)						Ref.	
	α-Fe ₂ O ₃ on Fe or S.S.	theoretical	685-680		525-515, 495	435-420	370	280-265	225	7
		experimental	655		510	429				8
		"	665-657		525-520, 495	435	370	290		7
	α-Cr ₂ O ₃ on Fe α-Cr ₂ O ₃ on Cr	theoretical	765-740	610, 600	535-525	445, 405		305		7
		"	770-740	610	530-520	445, 410, 405		305		9
		experimental	750-730	610, 600	530-525	445, 410, 405				9
		"	730	610	540	440, 400		300		10
	Fe ₃ O ₄ on S.S. NiO on Ni	experimental	690-685		550-525	~440		340-325		7
		experimental		600	600-582			395-380		8
		theoretical			620-580			370		11
	NiCr ₂ O ₄ on Ni	experimental			620-580			390-380		11
		experimental	700-690		590	~460				11

685-660 shift due to thickness effect 495, 370 LO longitudinal mode

Table III. — Analysis of IR reflectance spectra of oxide layers developed on 304 stainless steel.

T (°C)	1 (min)	5 (min)
900	a Cr ₂ O ₃ [†] MnCr ₂ O ₄ NiO SiO ₂	Cr ₂ O ₃ [†] MnCr ₂ O ₄ S ₂ SiO ₂
	b Cr ₂ O ₃ Fe ₂ O ₃ spinels	Cr ₂ O ₃ MnCr ₂ O ₄ S ₂ Fe ₂ O ₃
1000	a Cr ₂ O ₃ [†] MnCr ₂ O ₄ Fe ₂ O ₃ SiO ₂	Cr ₂ O ₃ [†] MnCr ₂ O ₄ S ₂ Fe ₂ O ₃ SiO ₂
	b Cr ₂ O ₃ MnCr ₂ O ₄ Fe ₂ O ₃	Cr ₂ O ₃ , spinels, Fe ₂ O ₃
1100	a *Cr ₂ O ₃ MnCr ₂ O ₄ S ₂ Fe ₂ O ₃	Cr ₂ O ₃ MnCr ₂ O ₄
	b Cr ₂ O ₃ Fe ₂ O ₃	Cr ₂ O ₃ MnCr ₂ O ₄ Fe ₂ O ₃
† Cr (VI)	* Cr ₂ O ₃ on the tops of layer	Cr ₂ O ₃ main phase

Surface treatment : a : polishing; b : etching
 S₂ : nickel ferrichromite (see text)
 SiO₂ and Cr(VI) are respectively revealed by bands respectively located at 1240 cm⁻¹ and in the 850-1000 cm⁻¹ range.

The experimental results relative to the analysis of the influence of the surface preparation on the composition of the oxide layers are listed in table III.

The oxidation mechanism of polished samples may be interpreted as follows:

Cr (III) oxides (Cr_2O_3 and chromite spinel probably MnCr_2O_4 according XRD and SIMS studies) are always detected at the beginning of the oxidation process. A second stage of the oxidation mechanism corresponds to the formation of another spinel phase identified by microprobe analysis as $\text{NiCr}_{2-x}\text{Fe}_x\text{O}_4$ or $\text{Ni}_{1-x}\text{Fe}_x\text{Cr}_{2-y}\text{Fe}_y\text{O}_4$ (called S_2), figure 3a.

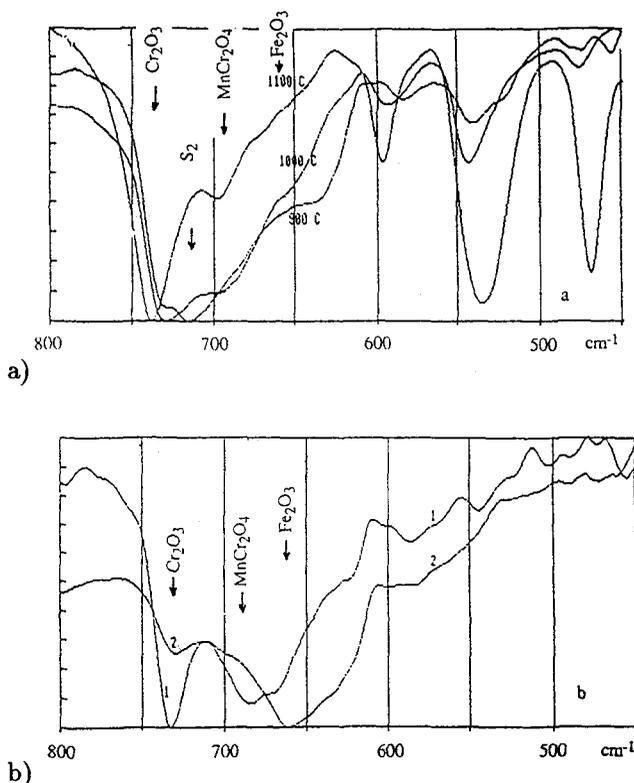


Fig. 3. — a) IR reflectance spectra of 304 AISI polished samples oxidized 1 mn at 900 °C, 1000 °C and 1100 °C (SR 80); b) Influence of surface treatments. IR reflectance spectra of 304 AISI polished (1) or etched (2) samples oxidized 1 min at 900 °C (SR 80).

The first stage of the oxidation mechanism differs when the surface is initially etched: $\alpha\text{Fe}_2\text{O}_3$ seems to be predominant instead of chromium compounds for polished samples, figure 3b.

3.2 MODIFICATION OF THE METALLIC PHASE AT THE METAL/OXIDE INTERFACE. — AISI 304 and 316 on stainless steels are normally austenitic (face centered cubic). But, when the surface of these materials is plastically deformed, a thin layer of martensite (body centered cubic) is formed on the austenite base [12, 13]. We observed this characteristic (CEMS and XRD) on our polished samples even though the chemically cleaned samples remained purely austenitic. The layer of martensite vanishes entirely after one hour of heat treatment at 700 °C in vacuum.

However, after oxidation treatments, the XRD spectra of AISI 304 and 316 stainless steels, either polished or chemically cleaned, show the presence of a bcc phase in addition to the oxides and austenite patterns. This b.c.c. phase becomes visible after 1 hour of oxidation at 900 °C, 5 min at 1000 °C and 1 min at 1100 °C. The intensity of the characteristic peaks grows with the oxidation time (Fig. 4). The lattice parameter of this phase ($a = 0.2860$ nm) is almost identical to that of the martensite obtained after polishing ($a = 0.2869$ nm) and is very close to that of α iron.

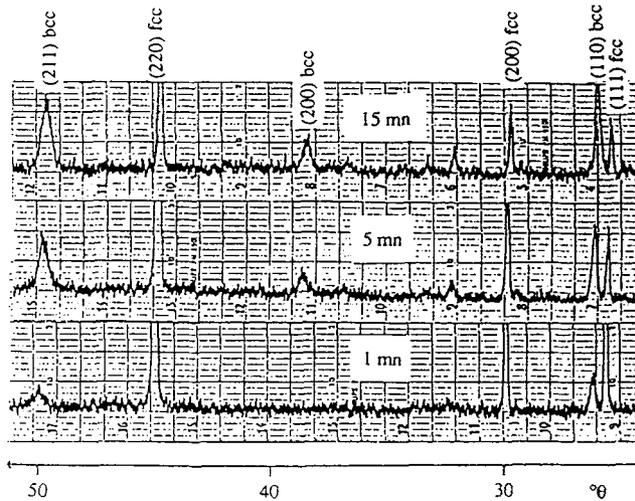


Fig. 4. — XRD spectra of AISI 304 at 1100 °C (polished samples).

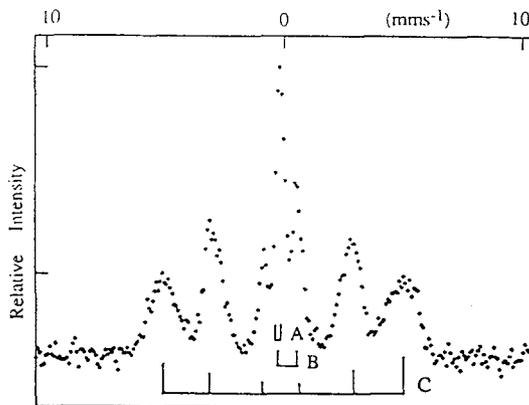


Fig. 5. — CEMS spectra of AISI 304 polished sample oxidized 1 mn at 1100 °C: A) fcc non magnetic; B) fine $\alpha\text{Fe}_2\text{O}_3$; C) bcc ferromagnetic.

After gradual abrasion of the oxide layer, the XRD spectra prove that the b.c.c. phase is located on the metallic substratum. A chemical etching removes it and leaves only the f.c.c.

austenitic phase.

The CEM spectra of some samples where the oxide layer was naturally thin or reduced by abrasion exhibit the superposition of a single peak characteristic of an austenitic stainless steel and a magnetic sextet which appears similar to that of the strain induced martensite, but the average hyperfine field ($\bar{H} = 320$ kOe) is higher than that (270 kOe) of the strain induced martensite [13, 14]. This magnetic sextet can be attributed to the b.c.c. phase mentioned before (Fig. 5).

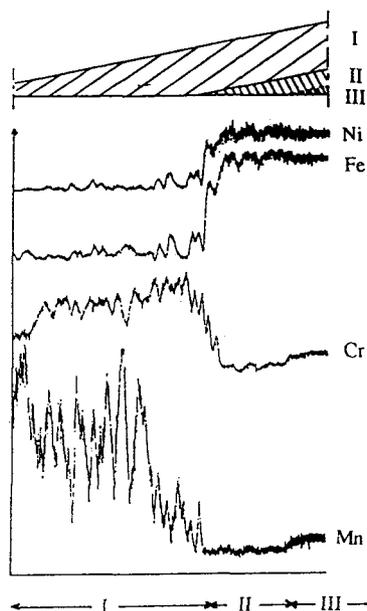


Fig. 6. — Microprobe analysis profiles of AISI 316 oxidized 15 mn at 1100 °C (obliquely cut sample): I) oxide layer; II) depleted zone of the metal; III) metal.

Table IV. — *Electron probe microanalysis of AISI 304 oxidized 15 mn at 1100 °C (obliquely cut sample): A) point of the metal near the oxide layer; B) point of the metal 20 μ m away from the oxide layer.*

	Si	Ni	Cr	Fe	Mn
A	0.06	11.89	10.35	77.50	0.20
B	0.50	8.89	18.03	71.10	1.48

In the same way, the electron probe microanalysis reveals in the metallic phase under the oxide a depletion of Mn and Cr. Figure 6 shows a microprobe analysis profile on the polished surface of an obliquely cut sample, and table IV compares the mass composition of a point of the metal at the metal/oxide interface with that of the bulk.

The modification of the chemical composition of the metal near the oxide layer can explain the values of the average hyperfine field observed in CEMS and is consistent with the results of Nagy *et al.* [15] who set a linear dependence of \bar{H} on the Cr content in FeCrNi alloys.

4. Conclusions.

The initial stages of the oxidation of 304 and 316 AISI steels in the range 900-1100 °C is quite similar. The surface preparation is an influential parameter: the chemical cleaning favors the formation of $\alpha\text{Fe}_2\text{O}_3$ and the mechanical polishing induces a formation of chromium oxides (Cr_2O_3 and chromite spinel phases).

As a result of the oxidation, the chemical composition of the adjacent thin layer metallic substrat changes in the way of a manganese and chromium depletion and induces a phase transformation γ (f.c.c.) \rightarrow α (b.c.c.).

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