

## ON THE OXIDE FORMATION ON STAINLESS STEELS AISI 304 AND INCOLOY 800H INVESTIGATED WITH XPS

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The influence of cold work on the initially formed oxide layer on the stainless steels AISI 304 and Incoloy 800H has been studied by XPS. Oxidations were performed at pressures of  $10^{-6}$ – $10^{-4}$  Pa and temperatures of 300–800 K. All samples showed a similar oxidation behaviour. The oxidation rates of iron and chromium are of the same order of magnitude at temperatures below 650 K. Subsequent oxidation results in an iron oxide on top of a chromium oxide layer. At temperatures above 650 K the metal surface becomes enriched in chromium, which is preferentially oxidized at these temperatures and pressures. Even prolonged oxidation does not result in an iron-rich oxide surface. Nickel has never been found in its oxidized form. The binding energy of oxygen, in the various oxide layers, is independent of the extent of oxidation and is 530.6 eV.

### 1. Introduction

In order to reach a better understanding of the influence of cold work on the initial oxidation behaviour of austenitic stainless steels it is necessary to obtain information on the composition of the oxide layers.

Previous studies [1–4] show a small influence of cold work on the oxidation behaviour of AISI 304 and Incoloy 800H under atmospheric [1,2] as well as under UHV [3,4] conditions. Cold work, however, does not seem to alter the mechanism of the oxidation but only to affect the diffusion rates in the oxide as well as in the metal and in this way influences the oxidation rate.

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Cold work has a small beneficial effect on AISI 304. Although the initial oxide layer is thicker than on an undeformed sample, the final oxidation rate is smaller. The effect of cold work on the initial oxidation behaviour of Incoloy 800H is only marginal and without practical importance. In spite of this small influence no differences have been found in the oxide compositions as monitored with AES.

The oxidation behaviour of stainless steels [1–3] and the elements Fe [14–18], Cr [19,20] and Ni [21–23] has been studied extensively in the past, with various techniques and under different experimental conditions. The complexity of the oxidation of iron itself makes it difficult to obtain a clear understanding of the oxide composition on stainless steels.

Brundle et al. [16] report that it is possible to characterize the iron oxides by XPS. The Fe(II) and Fe(III) states are distinguishable but octahedral and tetrahedral sites are not. At high oxygen partial pressures, iron is oxidized mostly to the Fe(III) state, while at low pressures the Fe(II) content increases. As reported in the literature [1–7], the oxidation of stainless steel at low oxygen pressures and low temperatures results in a layered oxide with an iron-rich outer layer and chromium-rich inner layer.

The aim of this study was to determine which oxides are formed and whether cold work affects the oxide composition on stainless steel.

## 2. Experimental

The chemical composition of AISI 304 (in wt%) is 17.4% Cr, 8.9% Ni, 1.3% Mn, 0.7% Si, 0.047% C, 0.017% S, balance Fe and that of Incoloy 800H (in wt%) 19.9% Cr, 31.7% Ni, 0.42% Ti, 0.7% Mn, 0.5% Si, 0.08% C, 0.085% S, balance Fe.

All samples were annealed at 1350 K for 1 h and water quenched prior to applying cold work. In this investigation undeformed samples were used as references. The following treatments were applied: 20% cold drawing and 75% cold rolling. Samples were cut by means of spark cutting. The damaged surface layer, induced by the spark cutting, was removed by grinding (220–800 grit SiC paper) and polishing (1  $\mu\text{m}$  diamond paste and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder). Before mounting in the UHV chamber (base pressure  $< 10^{-8}$  Pa), the samples were ultrasonically cleaned with isopropanol and acetone. Prior to all oxidation experiments the surface was cleaned by  $\text{Ar}^+$  ion bombardment ( $50^\circ$  with respect to the normal of the surface, 5 keV, 30  $\mu\text{A}/\text{cm}^2$ , sputter rate  $\sim 300$   $\text{\AA}/\text{min}$ ). In all XPS (VG ESCALAB) measurements  $\text{Al K}\alpha$  radiation (1486.6 eV) was used.

Oxidations were performed at pressures between  $3.0 \times 10^{-6}$  and  $5.0 \times 10^{-4}$  Pa and at temperatures between 300 and 875 K. Some oxidations were performed in successive steps of 20–30 s after which XPS spectra were taken.

Other oxidations were performed in one step of 1800 s. The composition profiles of the oxides were determined by means of XPS after successive Ar<sup>+</sup> ion sputtering. Standard spectra of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Johnson-Matthey (Specpure)), Fe<sub>3</sub>O<sub>4</sub> (Fisons (Laboratory reagent)) and chromite (Microanalysis Consultants Ltd., Cambridge) were taken in order to verify the states of iron in the oxidation process. Binding energies were measured relative to C1s at 284.6 eV.

### 3. Results

#### 3.1. Spectra of oxidized stainless steels

The XPS spectra of the successive oxidation stages of chromium and iron of an undeformed sample of Incoloy 800H at room temperature are given in fig. 1. The oxidation rates of iron and chromium are of the same order of magnitude; the metal-to-oxide ratio for chromium equals that iron. After

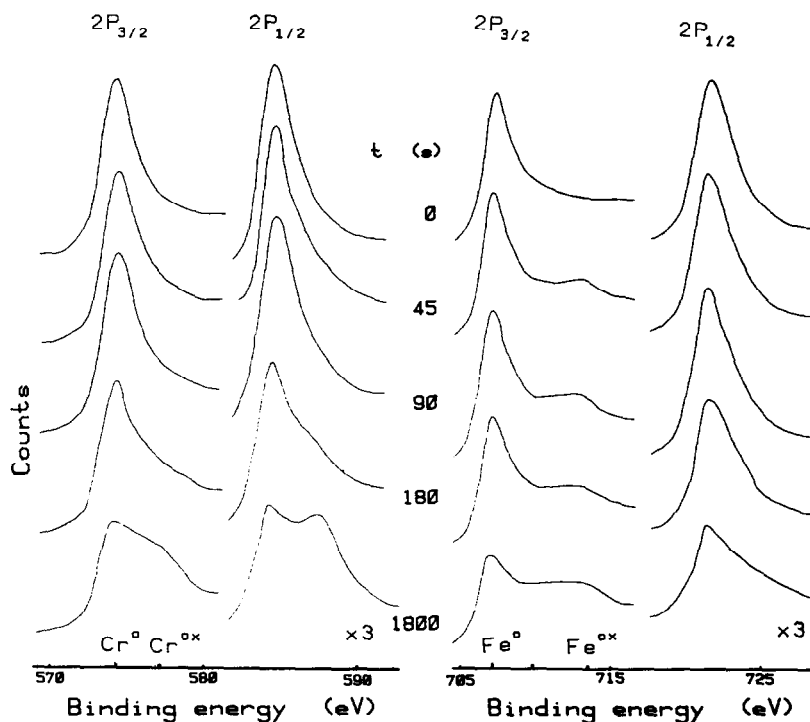


Fig. 1. Changes in the states of Cr and Fe as a result of exposure to oxygen ( $T = 300$  K,  $P_{O_2} = 4.0 \times 10^{-5}$  Pa, undeformed Incoloy 800H).

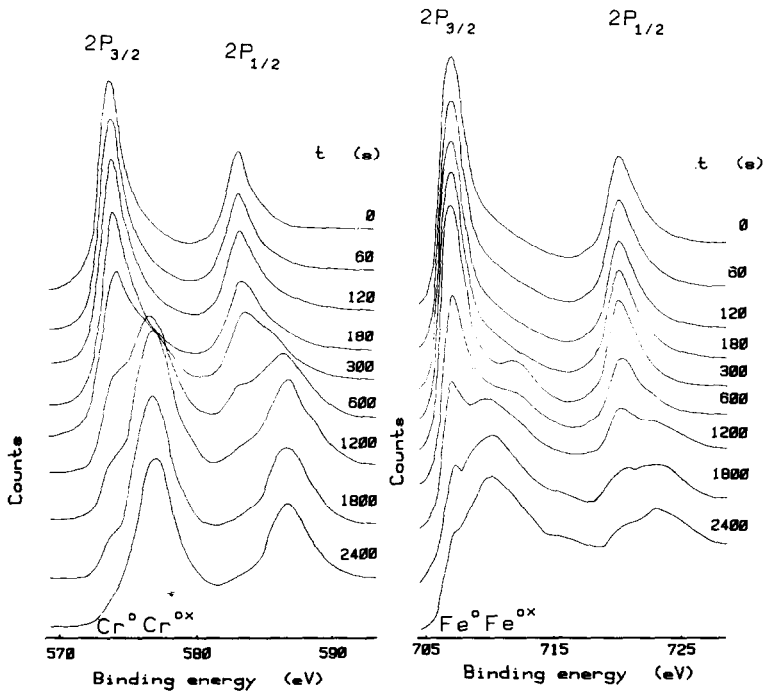


Fig. 2. Changes in the states of Cr and Fe as a result of exposure to oxygen ( $T = 570$  K,  $P_{O_2} = 2.0 \times 10^{-4}$  Pa, undeformed Incoloy 800H).

subsequent oxidation, however, a layered oxide is formed, in which the iron oxide is near the oxide/gas interface with a chromium oxide layer underneath.

Fig. 2 shows the XPS spectra of the successive stages of the high temperature oxidation ( $T = 570$  K) of undeformed Incoloy 800H. At high temperatures the metal surface becomes enriched in chromium (fig. 3), which is preferentially oxidized. The remaining oxygen content of 5 at% is probably due to oxygen dissolved in the surface layer. This is indicated by the absence of oxidized states of iron and chromium. A similar behaviour has been shown for Ni(100) by Hanekamp et al. [31]. In contrast with the low temperature oxidation iron oxide does not form a continuous layer on top of the chromium oxide; not even after longer exposures.

A low temperature oxidation and depth profile of undeformed AISI 304 is shown in fig. 4. As can be seen from fig. 4b, there is an iron-rich oxide near the gas/oxide and a chromium-rich oxide near the oxide/metal interface.

Nickel is not involved in the oxidation process as only metallic nickel has been detected throughout all oxidation experiments. In agreement with Brundle et al. [16] the oxygen binding energy is observed to be independent of the

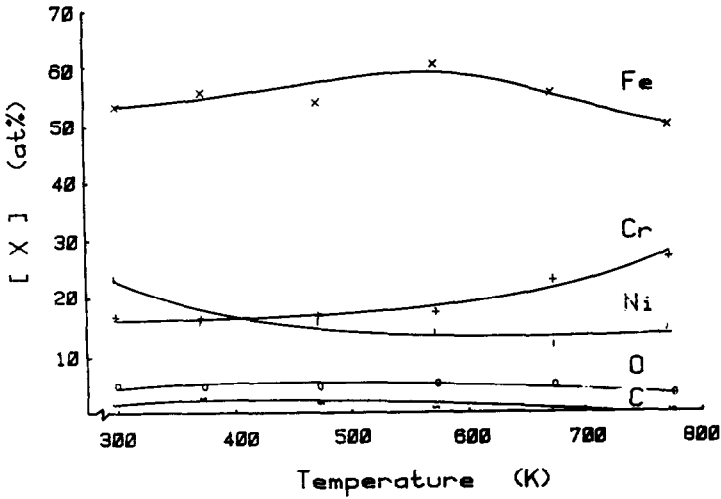


Fig. 3. Surface segregation (undeformed Incoloy 800H).

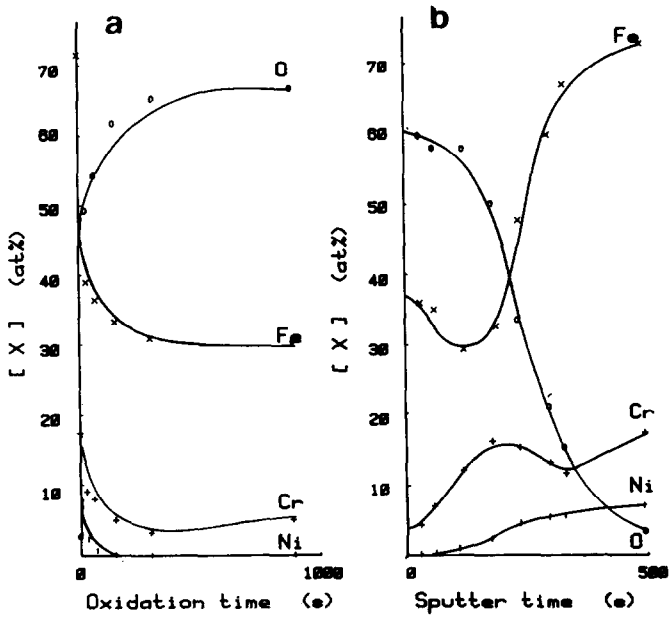


Fig. 4. (a) Oxidation of AISI 304 ( $T = 300$  K,  $P_{O_2} = 2.0 \times 10^{-6}$  Pa, rolled). (b) Sputter depth profile of (a).

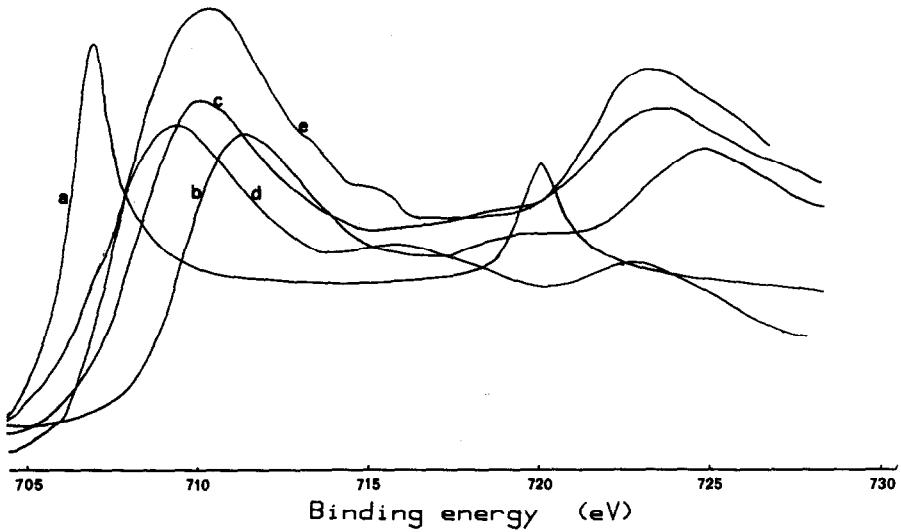


Fig. 5. Standard spectra of iron: (a)  $\text{Fe}^\circ$ , (b)  $\alpha\text{-Fe}_2\text{O}_3$ , (c)  $\text{Fe}_3\text{O}_4$ , (d)  $\text{FeO}$  [16], (e) Fe in chromite.

Table 1  
Binding energies of C, O, Cr, Fe and Ni

Element	BE (eV)	$\Delta\text{BE}(2p_{3/2}-2p_{1/2})$	Reference
C	284.6	-	[30]
O	530.6	-	[16], This work
	531.6	-	[30]
$\text{Cr}^\circ$	574.6	9.1	[30]
	574.4	9.1	This work
$\text{Cr(III)}$	576.6	9.7	[30]
	576.8	9.7	This work
$\text{Fe}^\circ$	706.6	13.2	[30]
	707.0	13.2	[16]
in AISI 304	706.6	13.2	This work
in Incoloy 800H	707.0	13.2	This work
$\text{Fe(II)}$ in $\text{FeO}$	709.7	13.6	[16]
	709.2	13.6	[29]
in chromite	710.3	13.1	This work
$\text{Fe(III)}$ $\gamma\text{-Fe}_2\text{O}_3$	711.2	13.6	[16]
$\alpha\text{-Fe}_2\text{O}_3$	710.7	13.6	[16]
$\alpha\text{-Fe}_2\text{O}_3$	711.2	13.6	This work
stainless steel	711.2	13.2	This work
$\text{Ni}^\circ$	852.3	17.4	This work
$\text{Ni(II)}$	853.3	18.4	[30]

oxidation state and it is not influenced by matrix effects either. It remains 530.6 eV throughout all experiments.

### 3.2. Spectra of pure Fe, $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeO and chromite

Fig. 5 gives the spectra of the possible oxidation states of iron as measured by XPS. Fig. 5a gives the spectrum of metallic Fe, figs. 5b to 5d give the spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeO. The spectrum of FeO has been taken from ref. [16]. Fig. 5e gives the spectrum of iron chromite.

Loss structure is observed in the spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and of chromite. The loss structure in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is very pronounced and corresponds with a binding energy of  $720.0 \pm 0.2$  eV. That in chromite is only very weak and corresponds with energies of  $713.3 \pm 0.2$  eV and  $715.2 \pm 0.2$  eV. In FeO it is situated at  $715.4 \pm 0.2$  eV; Fe<sub>3</sub>O<sub>4</sub> spectra do not show any clearly resolved loss structure.

The energy difference between the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states of oxidized iron in Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> is 13.6 eV, while that in chromite is only 13.1 eV.

Due to Ar<sup>+</sup> ion bombardment Fe(III) is reduced to Fe(II), in agreement with the results of Brundle et al. [16] and of Mitchell et al. [28].

The spectra of chromium show binding energies of 574.4 eV for the metallic state and 576.8 eV for the 2p<sub>3/2</sub> Cr(III) state. Table 1 gives a survey of the binding energies as measured by XPS.

## 4. Discussion

The spectra of iron in the oxide on stainless steel show some special features.

- (1) the energy difference between the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states is 13.2 eV throughout each oxidation experiment;
- (2) the reduction of oxidized iron, as a result of Ar<sup>+</sup> ion bombardment, does not show a shift of 1.5 eV as for pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> but one of only 0.2–0.5 eV;
- (3) the spectra do not show any loss structure.

A distinction can be made between the three different iron oxides by taking the binding energy of the oxidized iron with respect to that of metallic iron. The energy difference of Fe<sup>0</sup> and Fe(II) (in FeO) is  $3.1 \pm 0.2$  eV and that between Fe<sup>0</sup> and Fe(III) (in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is  $4.2 \pm 0.2$  eV.

Although FeO is unstable at low temperatures our recorded spectra of Fe<sup>2+</sup> show much resemblance to FeO spectra reported in the literature [16].

The formation of FeO or an oxide with an FeO like structure at low temperatures and low oxygen pressures might be due to the very thin oxide layers in our experiments or to an interaction between this thin layer and the metal substrate or to chromium incorporation.

Table 2  
Chemical shift of Fe as a result of exposure to oxygen

Material	Pretreatment	Oxidation conditions		Oxidation time (s)	Fe° BE (eV)	Fe <sup>ox</sup> BE (eV)	ΔBE (eV)	Suggested oxide	
		(K)	(Pa)						
AISI 304	20% drawn	300	$4 \times 10^{-6}$	1800	706.9	710.7	3.8	Fe <sub>3</sub> O <sub>4</sub>	
			$4 \times 10^{-4}$	60	706.8	709.9	3.1	FeO	
				120	706.6	710.3	3.7	Fe <sub>3</sub> O <sub>4</sub> /chromite	
				380	706.6	710.3	3.7		
				900	706.6	710.4	3.8		
			375	$4 \times 10^{-6}$	1800	706.9	710.6	3.7	Fe <sub>3</sub> O <sub>4</sub> /chromite
				$4 \times 10^{-4}$	30	706.5	710.3	3.8	
			475	$4 \times 10^{-4}$	30	706.7	709.6	2.9	FeO
					60	706.4	709.4	3.0	
					150	706.4	709.7	3.3	(FeO) <sub>1-x</sub> (Fe <sub>3</sub> O <sub>4</sub> )
					300	706.4	709.8	3.4	
				900	706.4	710.3	3.9	Fe <sub>3</sub> O <sub>4</sub> /chromite	
		575	$4 \times 10^{-4}$	30	706.5	709.6	3.1		
				90	706.7	709.8	3.1	FeO	
				300	706.6	709.7	3.1		
		675	$3 \times 10^{-5}$	120	706.6	709.6	3.0	FeO	
				300	706.5	709.5	3.0		
				600	706.7	709.7	3.0		
				180	706.5	709.9	3.4		
			$4 \times 10^{-4}$	300	706.5	709.8	3.3	Fe <sub>3</sub> O <sub>4</sub>	
				600	706.7	709.9	3.2		



Incoloy 800H	Undeformed	300	$5 \times 10^{-4}$	45-	707.0	711.1	4.1	Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub> Fe <sub>2</sub> O <sub>3</sub> FeO Fe <sub>3</sub> O <sub>4</sub> /chromite FeO/chromite Fe <sub>3</sub> O <sub>4</sub> FeO FeO/Fe <sub>3</sub> O <sub>4</sub> /chr. FeO/Fe <sub>3</sub> O <sub>4</sub>
				90	707.0	711.3	4.3	
				1800	707.0	711.3	4.3	
				1800	707.3	711.2	3.9	
				30	707.1	711.1	4.0	
				60	707.1	711.2	4.1	
				1800	707.1	711.1	4.0	
				30	707.3	710.4	3.1	
				60	706.9	710.3	3.4	
				300	707.0	710.6	3.6	
				300	707.4	710.0	2.6	
				600	706.8	710.0	3.2	
				1800	707.0	710.0	3.0	
				60	707.1	710.8	3.7	
				120	707.0	710.8	3.8	
				300	706.9	710.7	3.8	
				660	706.9	710.8	3.9	
				675	$4 \times 10^{-5}$	707.0	3.1	
				775	$4 \times 10^{-4}$	706.9	3.4	
				875	$4 \times 10^{-4}$	707.0	3.5	

If  $\text{Fe}_3\text{O}_4$ , in which both Fe(II) and Fe(III) occur, is present at the surface, the binding energy of iron is expected to shift between the value of Fe(II) and that of Fe(III). Thus the BE of Fe in  $\text{Fe}_3\text{O}_4$  should be  $710.5 \pm 0.2$  eV, which is 3.6 eV above metallic iron, and is almost the same as that measured for iron in chromite:  $710.3 \pm 0.2$  eV.

Even after very short oxygen exposure at low temperatures, iron in Incoloy 800H is oxidized mainly to  $\text{Fe}_2\text{O}_3$ . At higher temperatures ( $T \geq 475$  K) and low pressures FeO is formed, while at higher pressures ( $p_{\text{O}_2} \geq 10^{-4}$  Pa)  $\text{Fe}_3\text{O}_4$  or chromite is formed after prolonged oxidation.

Rolled Incoloy 800H shows a tendency for the formation of  $\text{Fe}_2\text{O}_3$  at all temperatures and pressures exceeding  $10^{-4}$  Pa, while at low pressures  $\text{Fe}_3\text{O}_4$  or chromite is formed. Drawn Incoloy 800H shows the formation of  $\text{Fe}_2\text{O}_3$  at low temperatures and very high temperatures (875 K), while at intermediate temperatures FeO and  $\text{Fe}_3\text{O}_4$  or chromite are formed.

In contrast with Incoloy 800H, AISI 304 does not form  $\text{Fe}_2\text{O}_3$  but only  $\text{Fe}_3\text{O}_4$  or FeO. Rolled AISI 304 shows the formation of a thick FeO layer, when oxidized at 575 K and at  $3 \times 10^{-5}$  Pa oxygen pressure. During high temperature oxidation ( $T \geq 775$  K) only chromium oxide is formed and neither metallic nor oxidized iron were detected. Drawn AISI 304 starts with the formation of FeO ( $p_{\text{O}_2} = 4 \times 10^{-4}$  Pa) which is oxidized to  $\text{Fe}_3\text{O}_4$  at longer exposures. At temperatures above 575 K only FeO is formed, while at pressures higher than  $10^{-4}$  Pa  $\text{Fe}_3\text{O}_4$  is formed even after a small exposure to oxygen.

Table 2 gives a survey of the stages of the oxidation of iron in stainless steels. The low temperature oxidation seems to be governed by the reactivity of the metals rather than by the thermodynamic properties of the oxides. At low temperatures chromium as well as iron oxides have been formed, although the standard free energy of formation ( $\Delta G_f^\circ$ ) of  $\text{Cr}_2\text{O}_3$  is far more negative than that for all other oxides involved. Betz et al. [25] conclude that the rapid growth of FeO, compared to that of  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  is the reason why FeO is formed at low temperatures. They report that in stainless steel the iron is oxidized at temperatures below 900 K while only at higher temperatures the first signs of chromium oxidation begin to appear. This is in contrast with the results shown in fig. 1, where the oxidation of iron and chromium start simultaneously. Depth profiles taken of samples oxidized at room temperature show an iron-rich layer on top of a chromium-rich oxide.

At temperatures above 800 K the stainless steel surface becomes enriched in chromium (fig. 3), which is preferentially oxidized. The low temperature oxidation behaviour implies a reaction mechanism in which iron oxide is reduced by chromium.

Adolphi and Muessig [11] suggest that initially islands of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are formed when AISI 304 is oxidized at temperatures below 675 K. Iron diffuses through the  $\text{Cr}_2\text{O}_3$  layer and forms  $\text{Fe}_3\text{O}_4$ . This is not supported by

the results presented in this paper, where it is shown (table 2) that even low temperature oxidation of AISI 304 may result in the formation of FeO. Ekelund and Leygraf [17,18] report that the initial oxidation is governed by the supply of Cr and Fe at the surface, which is limited by the diffusion of these elements in the steel matrix. Baer [27] was able to vary the oxide composition of AISI 304 at 1070 K from a uniform protective layer of  $\text{Cr}_2\text{O}_3$  to a non-protective  $\text{Fe}_x\text{O}_y$ , simply by altering the oxygen partial pressure. Our results, that at high temperature and low oxygen pressures only a uniform chromium oxide layer is formed, are in good agreement with this. Brundle et al. [16] could not distinguish  $\alpha\text{-Fe}_2\text{O}_3$  from  $\gamma\text{-Fe}_2\text{O}_3$ , from which they conclude that XPS and UPS techniques are not sensitive enough to detect the difference between the sites in which iron is situated. They report binding energies of  $\text{Fe}^\circ$ ,  $\text{Fe(II)}$  and  $\text{Fe(III)}$  of 707.0, 709.6 and 711.2 eV respectively, which are in good agreement with the binding energies reported in this paper. Coad and Cunningham [13] report a binding energy for  $\text{Fe}^\circ$  of 705.9 eV and for Fe in  $\text{Fe}_3\text{O}_4$  of 708.9 eV. A closer look at their figure 5 reveals a satellite peak at 6 eV above the  $2p_{3/2}$  peak of oxidized iron. Together with a energy difference of 3 eV between metallic and oxidized iron this spectrum is very similar to the spectrum of  $\text{Fe(II)}$  reported by Brundle et al. [16]. The FeO and  $\text{Fe}_2\text{O}_3$  spectra show small satellite peaks. The fine structure in the  $\text{Fe(II)}$  spectrum is situated at  $715.4 \pm 0.2$  eV, while that of  $\text{Fe(III)}$  lies at  $720.0 \pm 0.2$  eV. The values of FeO are very close to those for chromite, with its  $2p_{3/2}$  peak at  $710.3 \pm 0.2$  eV and a fine structure at  $715.2 \pm 0.2$  eV.

The iron spectra of oxidized stainless steels do not show any fine structure. This might be due to the thinness of the films ( $d \leq 60$  nm), to the presence of chromium, or to both. The fine structures in the chromite spectra are only very weak.

The results of Allen et al. [14] of pure iron show that the satellite structures only appear after long exposures ( $> 10^5$  L) and that the energy difference between the  $2p_{3/2}$  and  $2p_{1/2}$  states of iron varies from 13.2, after short exposures, to 13.6 eV after long exposures. This is in agreement with results reported in this paper. The oxides of iron formed on stainless steel show no fine structure and the energy difference between the two doublet states is 13.2 eV. These results point to the formation of a chromite,  $\text{FeCr}_2\text{O}_4$ , layer. However, sputter profiles show an iron enrichment at the surface which favours the formation of  $\text{Fe}_3\text{O}_4$ . It might be that chromite is formed at the interface between iron and chromium oxide. Mitchell et al. [28] report a shift in the  $\alpha\text{-Fe}_2\text{O}_3$  spectrum from 710.4 to 709.7 eV as a result of ion bombardment, from which they conclude that  $\text{Fe(III)}$  is reduced to  $\text{Fe(II)}$ , which is supported by our results.

In their LEED experiments with single crystal AISI 304, Adolphi and Muessig [11] only find FeO at temperatures above 1000 K in the (111) direction. On the (100) plane, however, they find a FeO spinel and on the

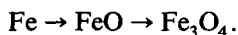
(110) plane they report the formation of an unordered FeO-like structure up to 770 K.

In the oxidation of iron, Allen et al. [14] suggest the following sequence  $\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$ , which of course will depend on temperature and oxygen partial pressure. Greyling and Roux [5] report that iron oxide is reduced by chromium. Betz et al. [25] suggest the reaction  $3\text{FeO} + 2\text{Cr} \rightarrow \text{Cr}_2\text{O}_3 + 3\text{Fe}$  to occur. This is supported by our results, which show that at room temperature iron and chromium are oxidized simultaneously at equal rates (fig. 1) while sputter profiles show a double layered oxide with iron oxide at the oxide/gas interface and chromium oxide at the oxide/metal interface.

The results presented in fig. 4b suggest some internal oxidation of chromium in the form of  $\text{Cr}_2\text{O}_3$ , because the nickel concentration reaches almost its bulk concentration even while a considerable amount of oxygen is still present.

## 5. Conclusions

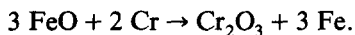
(i) The oxidation of AISI 304 results in the formation of iron oxide on top of a chromium oxide layer. The iron is oxidized in the same sequence as suggested by Allen et al. [14]:



(ii) The oxide compositions of AISI 304 are not influenced by cold work.

(iii) The oxidation of Incoloy 800H shows the formation of a double layer, with an outer layer of  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  and an inner layer of  $\text{Cr}_2\text{O}_3$ .

(iv) At low temperatures iron oxide is reduced by chromium according to the reaction suggested by Betz et al. [25]:



(v) In contrast with undeformed and cold drawn Incoloy 800H, where FeO is sometimes formed, only  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$  are observed on cold rolled Incoloy 800H.

(vi) Increasing temperature leads to segregation of chromium to the surface where it is oxidized preferentially.

(vii) The binding energy of oxygen is independent of the oxide formed and remains at 530.6 eV throughout each oxidation experiment.

(viii) Although XPS is a very sensitive technique, it was unable to distinguish between the spectra of iron in  $\text{Fe}_3\text{O}_4$  and in chromite. This is probably due to the very thin oxide layers which were examined.

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