University of Groningen

The effect of surface texture on the oxidation behaviour of polycrystalline Fe-Cr

Zijlstra, G.; de Jeer, L.; Ocelík, V.; De Hosson, J.T.M.

Published in:
Applied Surface Science

DOI:
[10.1016/j.apsusc.2018.08.036](https://doi.org/10.1016/j.apsusc.2018.08.036)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zijlstra, G., de Jeer, L., Ocelík, V., & De Hosson, J. T. M. (2018). The effect of surface texture on the oxidation behaviour of polycrystalline Fe-Cr. *Applied Surface Science*, 459, 459-467.
<https://doi.org/10.1016/j.apsusc.2018.08.036>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Full Length Article

The effect of surface texture on the oxidation behaviour of polycrystalline Fe-Cr

G. Zijlstra, L.T.H. de Jeer, V. Ocelík, J.Th.M. De Hosson*

Department of Applied Physics, Materials Innovation Institute and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ARTICLE INFO

Keywords:

Steel
Iron
Chromium
XRD
Atmospheric corrosion
EBSD

ABSTRACT

Grain-direction dependent oxidation at the surface of polycrystalline Fe-Cr steel is not well understood, as most of the described systems in literature focus on single crystals of either Fe or Cr. We found through electron backscatter diffraction that surface oxidation in air at temperatures between 260 and 450 °C depends severely on grain orientations at the outer surface. Subsequently electron microscopy was combined with X-ray photoelectron spectroscopy (XPS) and X-ray Diffraction (XRD) to characterize the oxide film further in detail. In particular we have observed the following sequence in oxidation rate of crystal planes parallel to the surface for Fe-Cr steel, $\{001\} < \{111\} & \{101\}$, which was not reported in literature before.

1. Introduction

The positive influence of chromium on the retardation of oxidation of iron has been noticed for almost two centuries. Pioneering work by Michael Faraday & James Stodart started in 1820 by alloying iron with noble metals [1]. Pierre Bertier followed with adding Chromium and developed Ferrochromium [2], which in turn inspired Faraday & Stodart to alloy with 3 wt% Chromium [3]. It was concluded in 1911 by Philip Monnartz that there is a steep drop in the corrosion rate when the alloy contains nearly 12 wt% of Cr [4].

Ferritic-martensitic (iron-chromium) steel is commonly used for plastic-casting moulds, cutlery and high precision components [5]. This category of steel is a trade-off between good forming and corrosion resistance, as the chromium content approaches the threshold of 12%. The bulk corrosion resistance depends critically on applied thermal treatments such as hardening and tempering, which promote either the dissolution or growth of chromium carbides [6–8]. The microstructure of the oxide layer on Fe-Cr steel as subjected to severe corrosion conditions was reported, e.g. the oxidation of steel under steam pipe conditions in wet and dry air at 600 °C of ferritic Fe-Cr and austenitic Fe-Cr-Ni 304L steel [9–11], and both types at a high temperature of 1000 °C [12]. The failure mechanism of a Fe-Cr-Ni steel at 700 °C in steam is presented in [13]. As the scale structure, growth and failure has been studied, no special attention was paid to the bulk grain orientation. The thickness of the oxide scales varied from 0.1 to 100 μm. Only one singular study focused on the orientation of oxides found on

polycrystalline Fe-Cr steel, with respect to the substrate [14]. Due to the high temperatures of 650–800 °C and a Cr content of 22%, mainly Cr-oxides were found. Scant work on pure polycrystalline iron revealed that after several hours oxidizing at 450 °C in air, mainly μm-thick magnetite-hematite duplex layers evolve, independent of the substrate microstructure [15].

It is well known that the protective passive layer on Fe-Cr steel consists of a mixed film of iron- and chromium oxides such as $(\text{Fe, Cr})_2\text{O}_3$ and $(\text{Fe, Cr})_3\text{O}_4$ [16], with a thickness of the order of several nanometers [17–19] before exposure to elevated temperatures. For an extensive background on the formation and properties of iron oxides as Fe_2O_3 and Fe_3O_4 reference is made to the reviews in [20–22] concerning the influence of point defects in these oxides. The formation of these oxides depends critically on the conditions such as oxygen pressure and temperature. Studies involving the particular oxide growth along the three main directions, i.e. $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, focus on e.g. iron [23,24], chromium [25–28] or Fe-Cr [29,30] single crystals, often under well-controlled laboratory conditions with precise amounts of oxygen at low pressure. The phase transformation between Fe_2O_3 and Fe_3O_4 has also been considered on deposited nano-layers [31,32].

The formation of thin oxide layers (passive films) has been formulated by Cabrera and Mott in 1949 [33]. This subject but also the work in relation to the crystal orientation has been extended by the reviews of Lawless [34] and Atkinson [35]. Although the influence of the crystal direction on the oxide is an old question, many disagreements between theory and experimental results exists. In a recent

* Corresponding author.

E-mail address: j.t.m.de.hosson@rug.nl (J.T.M. De Hosson).

interesting study by Takabatake et al. [33], polycrystalline iron with grains of several hundreds of micrometers was heated for one hour at 300 °C in air. The resulting oxide film had a thickness of about 150 nm, and was investigated with Raman spectroscopy and ellipsometry. It was found that the Fe_3O_4 : Fe_2O_3 ratio varied for different crystal orientations: the proportion of Fe_3O_4 in the oxide is in the order of $\{100\} > \{111\} > \{101\}$. Electrochemical tests indicate that for pure iron, the passive film formed at the same conditions on $\{110\}$ surface is thinner than on $\{100\}$ surface [36]. When we consider anodic dissolution of iron, the majority of cases show that the $\{100\}$ -oriented crystal faces exhibit the fastest rate of metal removal after electro-polishing or chemical polishing. The metal removal from the faces $\{101\}$ and $\{111\}$ seems to be similar in most cases [37]. Another study on polycrystalline iron was not conclusive: in one case the corrosion current increased for different crystal planes in the order $\{101\} < \{111\} < \{100\}$ for single grains, while in another study a dissolution rate of $\{100\} < \{111\} \sim \{101\}$ was obtained [38]. As for iron, also results on copper [39–41] do not provide unambiguous conclusions.

Do the systems reported in literature on single crystals apply, as steel used in service is in a polycrystalline form? Moreover, oxidation during daily use often takes place in ambient conditions, as opposed to laboratory conditions with very low oxygen pressure. In particular the initiation of corrosion in the early stages has still to be understood for ferritic-martensitic stainless steel with a minimum amount of Cr, as this stage might have an influence on the further oxidation progress. Therefore this work focusses on exposure in air for low temperatures, up to 450 °C. The resulting thin oxide film with a thickness below 100 nm demands a non-trivial approach, as study by cross-section is only (local) achievable by transmission electron microscopy. A combination of optical- and scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and X-ray Diffraction (XRD) is used to characterize the oxide film.

In this paper we concentrate on the influence of the different crystal orientation of the substrate of the polycrystalline stainless steel and its influence on the formation of the oxide layer. The aim is to investigate whether the substrate orientation has a predominant influence on the oxide layers; and the role of chromium compared with the results obtained for iron in literature.

2. Methods & materials

In this study we focus on a strip of polycrystalline stainless steel in the ferritic state of class AISI 420 with a chemical composition as listed in Table 1. The average grain size of the material is around 10 μm and contains a high amount of crystallographic texture due to rolling during the material manufacturing process.

Specimens were cut from the strip and mirror polished, where the final step included polishing with 0.25 μm diamond particles, resulting in a roughness with $R_a < 40$ nm. Colloidal water-based silica particle suspension was not used to avoid chemical etching. Exposure to water was also prevented by making use of an alcohol-type lubricant during polishing with diamond particles. After polishing, the specimens were rinsed with ethanol and dried in hot air. Recovery of the passive layer was executed in ambient conditions, i.e. at room temperature and 50% Relative Humidity, for at least 24 h.

The crystal orientation of the stainless steel substrate was detected by an electron back scatter diffraction (EBSD) system (EDAX Inc.,

Draper, Utah, USA) within a Field Emission Gun (FEG) Environmental Scanning Electron Microscope (ESEM) (Philips, The Netherlands). By adding markers in the area of interest through micro-indentations, the same area prior and after the recovery of the passive layer was analyzed. Both the polished and recovered surfaces were still suitable for EBSD examinations. The area of interest has a size of $250 \times 200 \mu\text{m}^2$ and was scanned in a hexagonal grid with a step size of 0.4 μm , using an acceleration voltage of 30 kV. EBSD data were analysed by using the TSL OIM Analysis 7.3 software. Grain boundaries were defined for a misorientation angle larger than 5°.

The corrosion films were established by oxidizing the mirror polished and recovered surfaces in air. The specimens were put in a quartz tube with openings at both ends and were introduced into a heat induction furnace (ThermoFisher, Waltham, Massachusetts, USA). Temperature was measured with a thermocouple placed inside the quartz tube, and kept constant within ± 5 °C. Oxide layers were grown by a series of heat treatments. The applied temperatures are typical used at annealing for stress relieve, and well above the 200 °C to stimulate Fe diffusion to the surface [43]. First, the specimen was kept at 260 °C for 20 min. Thereafter the specimen was brought subsequently to 300, 350, 400 and 450 °C, with a dwell time of 20 min at each temperature (see Table 2). After each oxidation step the specimen was taken out of the furnace for observation with the optical microscope. The area of interest, prior indexed by EBSD, was investigated with an Olympus VANOX-T optical microscope (Olympus, Tokyo, Japan), making use of the indentations as markers.

XPS was performed with a Surface Science SSX-100 ESCA, operating with a monochromatic Al K α X-ray source. Sputter removal (bombarding) took place using Ar⁺ ions of 2 kV, under a 50° degree angle of incidence with the normal of the specimen surface.

For the characterization of the layer build-up of the oxidized specimens, both classical X-ray Diffraction (XRD) (Brukers, Billerica, Massachusetts, USA) as well as grazing incidence XRD (GIXRD) (PANalytical, Almelo, The Netherlands) operating with Cu anodes, were performed. With XRD crystal orientations and crystallographic phase of the bulk were measured. With GIXRD the angle of incidence is so small that information at limited depth is obtained. The phase and distribution of the crystal orientations were measured from the outermost layer of the specimen. Information of the formed oxide layer was retrieved accordingly. In contrast to EBSD, the XRD methods do not give spatial information, but only the volume averaged crystallographic information over a large area.

3. Results

3.1. Thin film interference – grain orientation

A palette of various colours is obtained at the surface due to the thermal treatments, as shown in Figs. 1 and 2. The colour originates from the oxide layer by thin film interference, where the thickness of the layer controls the interference at certain wavelengths. The thickness of the oxide layer depends on the oxidation temperature and exposure time [44–46]. The order from thin to thicker oxide layers is: straw yellow, brown yellow, rosy mauve, blue [44], see Fig. 3. An oxide thickness of 35 nm (straw yellow) and 59 nm (blue) has been obtained

Table 2

Heat treatment of the different samples used for the comparison of relative oxide thickness and crystal orientation.

Oxidation step	Heat treatment	
1		260 °C for 20 min
2	After step 1	+ 300 °C for 20 min
3	After step 2	+ 350 °C for 20 min
4	After step 3	+ 400 °C for 20 min
5	After step 4	+ 450 °C for 20 min

Table 1

Chemical composition of AISI 420 class of martensitic stainless steel (wt%) [42].

C	Cr	Si	Mn	P	S	Fe
Min. 0.15	12–14	1	1	0.04	0.030	Bal.

Fig. 1. Two sequences (area I & II) of local change in colour due to oxidation. Each sequence shows (a) a $[001]$ inverse pole figure map and the light microscopy image of the same area after heating at (b) 260 °C; (c) 260, 300 °C; (d) 260, 300, 350 °C; (e) 260, 300, 350, 400 °C and (f) 260, 300, 350, 400, 450 °C, for 20 min at each temperature (also described in Table 2) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

for iron by [45], and 46 & 72 nm for straw & blue by [47]. This general colour scheme/order can also be recognized in Fig. 1. Within each image, local colour differences are noticed: the general coloured surface is decorated with small areas with a deviating colour. The particular areas remain deviating in colour throughout the tempering scheme of Fig. 3. The deviating areas are attributed to a thinner oxide layer compared to the remaining surface. The difference is estimated to be in the order of several nm. The surface colour can be a combination of oxide thickness and surface morphology. Differences in surface structures as in [14] were not seen. Large sized nodules up to almost 1 μm as in [46] were not found either. Small spheres of about 100 nm, however, cover the surface. In any case, the deviating areas are lacking behind in the corrosion scheme compared to the rest of the surface.

When these areas are compared to the $[001]$ inverse pole figure (IPF) map on the crystal plane parallel to the specimen surface, it is noticed that they correspond to particular crystal planes parallel to the surface. On a local level this is observed very clearly.

The deviating areas have the same size and shape as the grains with the $\{100\}$ planes on the surface (red/orange grains in Fig. 1a). Not only “pure”, but also orientations close to $\{100\}$ planes show a lack of

oxidation. The surface after oxidation step 5, shown in Fig. 1f, is different compared to oxidation step 1–4. Here three main colours can be distinguished: dark red, dark blue, light blue. The intense light blue grains, which are the most oxidized, correspond to the grains with $\{101\}$ planes (in green) of Fig. 1a. The dark red spots correspond to the $\{100\}$ grains, however they are not homogeneously coloured and partly decorated by ridges of blue oxide spheres. There are two reasons to exclude that the orientation of the planes at the surface are influencing the reflectivity and therefore the brightness of individual grains.

First, no difference in brightness between the grains are observed on a fresh polished surface, but after short oxidation it is seen (Fig. 1b). Second, these particular $\{100\}$ grains should also be brighter in the final oxidation step in Fig. 1f, which is not the case. A similar observation was confirmed on a more global scale in Fig. 2 and therefore the correlation between surface crystal plane and its degree of oxidation is not due to local effects. In Fig. 2 for each oxidation step the global microstructure is seen with the grain boundaries highlighted. The colour of the grains for different oriented planes is schematically depicted in Fig. 3. Hence the relative oxidation speed of the particular grain orientations can be categorized in two stages. Figs. 1 and 2 show

Fig. 2. (a) $[001]$ inverse pole figure map of the global area of interest. Optical images with EBSD grain boundaries superimposed after heating at (b) 260 °C; (c) 260, 300 °C; (d) 260, 300, 350 °C; (e) 260, 300, 350, 400 °C and (f) 260, 300, 350, 400, 450 °C, for 20 min at each temperature. The superimposed boundaries are varied in colour to enhance the contrast of the boundaries and the microstructure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Colour change of the grain due to increase of oxide thickness according to [44–46]. The colour of the grains with different oriented planes is placed in the colour sequence for two stages of the oxidation process as seen in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

snapshots of the oxidation at discrete temperatures. The different oxidation processes change gradually whereby the first stage is mainly present up to 350 °C; the second stage is most pronounced at 450 °C.

- At the first stage of oxidation the system is split in {0 0 1} planes lacking behind while {1 1 1} & {1 0 1} both progressing more: {0 0 1} < {1 1 1} & {1 0 1}.
- The second stage of oxidation is split into a threefold system with {0 0 1} planes still behind but {1 0 1} more progressed than {1 1 1}: {0 0 1} < {1 1 1} < {1 0 1}.

In Fig. 4 an area of $240 \times 240 \mu\text{m}^2$ shows that stage 1 oxidation is not a local or an incidental phenomenon, but observed on a global scale. The clearly visible deviating areas again coincide with the grains with {1 0 0} planes parallel to the surface, underlining their relation. Darker patches are also observed where the colour difference is caused by the lack of carbides on the surface in these areas. The carbides have a high reflection, which is facile observed with the optical microscope at high (100×) magnification, contributing to a lighter or darker perception of the area. There is no relation between these patches and the orientation of the grains.

3.2. Oxide chemical composition

In order to characterize the chemical composition of the oxide layer, a specimen was oxidized for 20 min at 300 °C in air. An XPS depth-profile was obtained by alternating measurements and sputtering of the surface by Ar ions. A selection of the Fe-2p spectra with increasing sputtering time is shown in Fig. 5. The initial –not Ar ion etched– surface shows a Fe-2p spectrum with the Fe-2p_{3/2} peak position around 711.3 eV and a satellite peak at around 720 eV, which is associated to the Fe³⁺ valence and therefore the chemical compound Fe₂O₃ oxide

Fig. 5. Fe-2p XPS spectra after Ar etching for 0, 20, 110, 210 and 345 min, from a specimen oxidized for 20 min at 300 °C. Observed is the transition from Fe³⁺ (0 min.) to fully metallic Fe (345 min.).

[48,49]. After 20 min of etching the satellite at 720 eV vanished, but it reappears at 716 eV after 110 min. In the latter structure, where the Fe 2p_{3/2} peak position also shifts towards 710.5 eV a structure containing Fe²⁺ valence is detected. A structure containing solely Fe²⁺, e.g. Wüstite (FeO), also shows a satellite at 715.5 eV, but also a main peak at 709.5 eV [48,49]. Magnetite (Fe₃O₄) has a main peak at 710.6 eV, but no clear satellite peak [48,49]. The clear spectrum after 345 min etching has a peak at 707.4 eV, which agrees very well to metallic Fe; it indicates that the oxide layer has been removed and the bulk/substrate is reached. Therefore it is clear that the spectrum from the surface

Fig. 4. Specimen surface after sequential heating at 260, 300 and 350 °C for 20 min at each temperature. (a) {0 0 1} Inverse Pole Figure with grain boundaries (white) on which the different crystal plane orientation parallel to the surface of the substrate are shown. (b) Light microscopy image on which a difference in degree of oxidation is observed on the surface. A good correlation between the grain with a {0 0 1} plane on the surface and the lighter degree of oxidation is observed. Furthermore, {0 1 1} and {1 1 1} planes have a similar degree of oxidation.

matches very well to Fe_2O_3 , and the spectrum at the end of the oxide layer to (bulk) metallic Fe, however in-between additional (satellite) peaks are observed which is an artefact of the argon ion etching, whereby Fe^{3+} is chemical reduced to Fe^{2+} and preferential sputtering of O can take place. It is demonstrated in [50] how an XPS spectrum can change by sputtering of pure Fe_2O_3 , in which the first three stadia of the depth profile as seen in Fig. 5 can also be recognized. It is important to mention that the magnetite can be written as $\text{FeO}\cdot\text{Fe}_2\text{O}_3$, however since Wüstite is only stable at a temperature above 550 °C [20], and because the thin oxide layer causes a low oxygen activity on the bulk interface due to fast iron transport, it is not likely to be present. Pure magnetite is an inverse spinel with divalent and trivalent Fe and describes as $\text{Fe}^{3+}(\text{Fe}^{3+}\text{Fe}^{2+})\text{O}_4$ [51,52]. In contrast Chromite, FeCr_2O_4 is a normal spinel with $\text{Fe}^{2+}(\text{Cr}^{3+})_2\text{O}_4$. Due to the relative abundance of Fe, it is more likely that Cr inhibited in the spinel will be present in an inverse spinel of $\text{Fe}^{3+}(\text{Cr}^{3+}\text{Fe}^{2+})\text{O}_4$ [53]. It has been shown that XPS spectra can be deconvoluted to resolve the Fe-2p [54] spectra, but in this work they cannot provide a conclusive answer to the question which specific iron oxide are present in the core of the oxide layer as the oxides can contain both Fe^{2+} and Fe^{3+} . Therefore, we turn to the quantitative information from the elemental distribution ratio.

The normalized peak intensities as a function of the sputtering time for Fe, Cr and O, which are the three main elements found in the oxide layer, are plotted in Fig. 6. This elemental depth-profile is constructed by the summation of all valence peaks of each individual element, e.g. the full Fe-2p_{3/2} peak. No other elements were detected; except for carbon which is only present in small quantities in the carbides, grain boundaries and as contamination on the surface. At the initial oxide/gas interface ($t = 0$ min.) a relative high concentration of oxygen is present. This can be due to carbon contamination, but it is also likely that hydroxide groups are present [55,56]. After 10 min of sputtering these groups were removed. Up to $t = 100$ min. the iron/oxygen ratio is about 40/60, indicating presence of the structure Fe_2O_3 . The following decrease of O content and increase of Fe suggests a shift towards the inverse spinel Fe_3O_4 . At $t = 160$ min a small peak of metallic Fe is noticed, which increases as the bulk is reached (see Fig. 5). The contribution of this peak increases the relative intensity of iron in Fig. 6, troubling the determination of iron oxide structure. Finally, a Cr enrichment peaking after 300 min is observed, just before the substrate–oxide interphase. Therefore, the general distribution of elements in this early stage is already similar to those observed in thicker oxide

layers [9,10].

It must be noted that the XPS provides information over a depth of 5–10 nm. Therefore, acquired information from layers of specific oxide structures of only several nm thick, will be accompanied by signals from the surrounding layers. The lateral resolution is limited by the spot size of 600 μm in diameter. The retrieved signal contains therefore in our case the information of the surface of several thousands of grains. It is concluded that on average after heating at 300 °C the outer layer consist of Fe_2O_3 , which is about 1/3 of the total oxide thickness.

3.3. Oxide structural composition

We have examined in detail the crystallography and crystal phases with XRD and GIXRD. Both X-ray methods give us global information about the crystallographic phases present, in contrast to the EBSD measurement which gives primarily local information. The crystallinity and texture of the substrate was measured with powder-XRD and was used as a reference measurement. For the phase and crystallinity information of the grown oxide layer we performed GIXRD measurements after short tempering, 20 min at 300 °C (yellow surface), and after long tempering procedure, oxidized up to 450 °C (purple surface) with the same treatment as oxidation step 5 in Table 2. The information depth was varied by changing the incident angles; we used three different incident angles 0.25°, 0.33° and 0.50° corresponding to an information depth of 18, 24 and 37 nm, respectively.

The GIXRD spectra for both specimens are shown in Fig. 7 for both the short tempered (yellow) and long tempered (purple) specimens with the corresponding crystal planes of the phases present. For the short tempered specimen the peak positions and intensities for the different depths are similar. However, small differences in peak intensities are observed for peak 1 and 3, whilst peak 2 has a constant intensity. The inset in Fig. 7a is a magnification of peak 3 and shows a clear increase of peak height with increasing incident angle. Peak 1 and peak 3 correspond to both the Fe_{bcc} as well as the Fe_3O_4 phase. Whilst both the $(\text{Fe-Cr})_{\text{bcc}}$ substrate and the Fe_3O_4 give diffraction peaks at similar angles, by removing the background we observed that the peak positions agree better with Fe_3O_4 than the $(\text{Fe-Cr})_{\text{bcc}}$ phase. Moreover, the relative peak intensity for the three peaks differs from the bulk measurement performed by powder XRD. This difference is in agreement with an additional magnetite top layer on the substrate. The normalized intensity peaks seen in the inset of Fig. 7a show an increase of the Fe_3O_4 fraction with decreasing incidence angle. It is therefore concluded that the measured oxide film is very thin and a large part of the information is measured from the oxide-substrate interface.

The GIXRD spectra reveal that the oxide layer of the purple surface is more developed compared to the short tempered yellow specimen due to the clear presence of crystalline Fe_2O_3 and Fe_3O_4 phases. Fig. 7b shows a more distinct change in diffraction spectrum with depth than the short tempered specimen with more peaks. Again, we observe a difference in the relative peak intensities for the peaks at 44.8, 65.2 and 82.5° 2 θ compared to the substrate measurement; thereby confirming a magnetite layer. The additional peaks are all attributed to the formed hematite layer due to the extra oxidation steps. The hematite crystals grow according to a specific orientation relation on the crystalline magnetite surface therefore only specific hematite crystal planes are measured. Because the polycrystalline stainless steel substrate is highly crystallographic textured, some magnetite and hematite crystal orientations are more pronounced present than others, due to the orientation relationship (OR) between substrate and magnetite, and a second OR between the hematite grown on magnetite. These orientation relationships for a pure Fe system with its oxidation products was already demonstrated for single crystals in [57].

In our analysis of a polycrystalline Fe-Cr system two oxide phases were found; an overview is presented in Table 3. Cr can be present in the inverse spinel as well as Cr_2O_3 with the corundum hexagonal structure, however this phase has not been detected here. These Cr

Fig. 6. XPS depth profile of the surface, after tempering for 20 min at 300 °C in air. The top layer ($t = 0$ –100 min.) consist mainly of iron oxide, presumably Fe_2O_3 with a Fe/O ratio of 40/60; a chromium enrichment is observed before bulk composition values are reached ($t = 345$ min.). The intensity of each element is the summation of all valence peaks.

Fig. 7. Phase and crystallographic information of the top oxide layer measured by GIXRD at different incident angles (0.25°, 0.33° and 0.50°) which correspond with a maximum information depth of 18, 24 and 37 nm, respectively. (a) GIXRD spectrum for the yellow specimen. The composition up to a depth of 37 nm has no significant change in layer composition. Moreover, the amounts of oxide products (magnetite and hematite) are hardly present at all. The inset shows a magnification of peak 3. (b) GIXRD spectrum for the purple specimen. The amount of oxide products (magnetite and hematite) are well detectable, however the amounts do not vary a lot. A significant difference in background signal is observable due to a change in the amorphous/crystalline ratio.

Table 3

Phases found on oxidized polycrystalline Fe-Cr steel, as detected in Fig. 7.

Phase	Crystal plane surface
Fe-Cr _{bcc}	(1 0 1); (2 0 0); (2 1 1)
Fe ₃ O ₄	(2 2 2); (4 0 0); (4 0 4); (4 4 4)
Fe ₂ O ₃	(2 1 1); (3 1 2); (3 3 2); (4 3 3)

containing phases have a similar diffraction spectrum as the iron oxide phases, however in the GIXRD results in this work the Cr phases show a worse agreement with the expected peak position than Fe₃O₄ and Fe₂O₃. Furthermore, considering the maximum information depth of 37 nm at an incidence angle of 0.5°, it is likely that the Cr-enriched layer close to the metal/oxide interphase (as seen in Fig. 6) is not reached. The total oxide thickness of a purple oxidized Fe specimen suggests a total oxide thickness of 59–150 nm [44,47,58]. With increasing angle of incidence, i.e. deeper in the oxide layer, we see that the intensity of the peaks corresponding to Fe₃O₄ (2 2 2) as well as

Fe₂O₃ (2 1 1) decreases, and Fe₂O₃ (3 1 2) decreases significantly; the intensity of the peak corresponding to Fe₂O₃ (4 3 3) decreases and almost vanishes.

4. Discussion

For polycrystalline stainless steel we observed a similar build-up of the oxidation layer as found in Fe systems: the short tempered (yellow) specimen at 300 °C, XPS results indicate both the outer hematite and inner magnetite layer. However, the GIXRD results show mainly the peaks of the {1 1 1} magnetite crystal planes, where also multiple peaks for hematite were expected. This suggests that magnetite with a {1 1 1} crystal plane parallel to the surface is the only magnetite which grows crystalline on the polycrystalline surface, without a relation to the bulk grain orientation. The lack of detected hematite in the GIXRD results, despite the hematite outer layer found by XPS, is attributed to the non-epitaxial growth of the hematite on the {1 1 1} magnetite [57], as well as the possible amorphous state of hematite. Amorphous or nano-crystalline domains cannot be detected by GIXRD.

On the purple specimen, which was heated with a final temperature of 450 °C, both magnetite and hematite were detected by GIXRD, as summarized in Table 3. When we compare the crystallographic information to the results of oxidation of magnetite single crystals by Zhou et al. [57], as shown in Table 4; we conclude that the hematite phases found in this work correspond mainly to the oxidation products found on {1 1 1} magnetite. Similar in literature, after heating several hours at 450 °C, also a double layer was found, though with a very small top layer of hematite, compared to magnetite [15]. Also after continued heating, the magnetite sub-layer grew faster than the hematite top layer.

Notwithstanding the importance of the oxidation process on the surface of complex materials as polycrystalline stainless steel rather scant literature was found on the detailed relationship between the crystallography and microstructure of the substrate. However, comparable work was performed to relate the crystallography of Fe based substrates with the thickness and crystallography of the oxidation products.

Vernon [43] showed that for pure Fe oxidized in air a double layer was formed of an inner magnetite and outer hematite layer at 200 °C. Zhou [57] studied the oxidation of magnetite at 300 °C; it was concluded that the formation of hematite on (1 0 0) and (1 1 1) magnetite was not epitaxial; for (1 1 0) magnetite it was unlikely to be epitaxial. The work as presented in literature raises the question whether the same relationship holds for Fe-Cr based systems and whether crystallography of the different layers can be related to each other. For single crystal magnetite specifically oriented hematite crystals form on the differently orientated crystal planes, as listed in Table 4. For temperatures above 600 °C the oxidation film consists of a mixture of iron oxides, where Wüstite, magnetite and hematite are present. A layer by layer growth is observed on polycrystalline Fe for a pressure of 2×10^{-4} mbar at 500 °C, whilst for 700 °C island growth is observed due to Wüstite formation [59]. The question that arises for polycrystalline Fe-Cr steel is whether there is an orientation relationship (OR) between the substrate and the inner magnetite; and the magnetite and the outer hematite. Moreover, are there prevalent atomic planes which dominate the oxidation kinetics?

The oxidation rate on an α -Fe substrate depends on the crystal plane

Table 4

Iron oxide phases found on magnetite single crystals, from Zhou et al. [57].

Magnetite	Fe ₃ O ₄	Fe ₂ O ₃
(1 0 0)	(4 0 0)	(1 2 0); (1 3 2)
(1 1 0)	(2 2 0); (4 4 0)	(-2 1 1)
(1 1 1)	(2 2 2); (4 4 4)	(1 2 1); (1 3 2); (3 4 3)

at the surface: in decreasing order of oxidation rate that is $\{001\} > \{111\} > \{011\} > \{320\}$ [60,61], which is opposite to the results found on our polycrystalline stainless steel in phase II. A less dense packed crystal plane at the surface is more susceptible to oxidation than a dense packed plane, because diffusion from and into the substrate is more likely. In contrast, it is shown for Fe at 500 °C that planes with an higher atom density exhibit faster oxidation kinetics in the initial oxidation reaction [59]. The diffusion rate of Fe to the surface is around $1\text{--}2 \times 10^{-15} \text{ cm}^2/\text{s}$ [61]. For the case of iron, at 250 °C and a low O_2 pressure a pure magnetite layer is formed on all planes; whilst at 550 °C for a higher O_2 pressure the oxidation film consists of an inner magnetite and outer hematite layer; the found OR for this layer was $\{001\}_{\text{Fe}}||\{001\}_{\text{M}}||\{114\}_{\text{H}}$ [62]. The growth rate of the hematite cap layer on the different magnetite planes (and therefore the oxidation speed) was ordered as $(100) > (110) > (111)$ [57]. Therefore, the oxidation mechanism is not to be expected similar for polycrystalline stainless steel compared to iron.

Study on the initial oxidation at low pressures ($\sim 10^{-8}$ mbar) of Fe-Cr single crystals with chemical composition close to the material in this work gives us an insight in the influence of particular crystal planes at the surface when Cr is involved. At room temperature oxidation starts with an initial Cr oxide layer followed by an iron oxide layer, whereby these thin oxide layers do not seem to have a “three-dimensional periodicity” [63]. If the oxidation takes place at 527 °C, also an initial Cr oxide layer is formed. The later formed iron oxide outer layer on the (100) crystal is a normal or inverse spinel-type phase with fcc symmetry, however no ordering is found on the (110) crystal [63].

It has to be emphasized that the magnetite layer does not grow directly on the Fe-Cr stainless steel, but rather on the passive layer present prior to the tempering treatment. This new finding for the Fe-Cr steel is a major difference compared to a Fe-system. As indicated by the XPS profile in Fig. 6, the passive layer is an (Fe, Cr)-oxide which is too thin to be detected by SEM, EBSD and GIXRD. Moreover, FeOOH could be present at the start of the tempering treatments, which decomposes to form Fe_2O_3 with increasing temperature.

Magnetite has the inverse spinel structure at low temperatures with an fcc oxygen sub-lattice structure. This means that all ions of Fe^{2+} valence and half of the Fe^{3+} occupy the octahedral sites and half of the Fe^{3+} occupy the tetrahedral sites [51,52]. Magnetite $\{111\}$ planes therefore consist of octahedral and mixed octahedral/tetrahedral located atoms along the $\langle 111 \rangle$ direction. A relationship between oxidation rate and dense packed planes can be retrieved, namely that more dense packed planes are more susceptible for oxidation. Magnetite has a Verwey transition around -153 °C, above this temperature it will act as a half metal with mobile electrons. Therefore it is treated as one type of Fe without valence difference and their behavior is considered identical [64,65].

The attributed mechanism for oxidation of magnetite is mainly diffusion of iron cations by Zhou et al. [57], in which the diffusion constant is greater for $\langle 100 \rangle$ than along $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. In contrast, our observation is that at temperatures < 400 °C the oxidation rate for the different crystal planes of the Fe-Cr substrate are in an increasing order $\{001\} < \{111\} \& \{110\}$, which would mean that the dense packed planes are more susceptible to oxidation. Pöter et al. [59] showed that in the initial oxidation phase diffusion of cations from the bulk through the oxidation layer is faster than oxygen from the gas phase to the metal phase. For higher temperatures, and therefore also larger diffusion times, we observed a further distinction between oxidation rate and crystal planes of the substrate: $\{001\} < \{111\} < \{110\}$. Given that the OR in Table 5 is correct and the presence of the magnetite layer on the substrate at temperatures > 400 °C, the following relation of oxidation rate and crystal planes of the magnetite can be deducted: $\{001\} < \{210\} < \{111\}$, which agrees with our GIXRD results.

For the diffusion of Fe towards the surface, the respective diffusion constant through the different oxide products, magnetite and hematite,

Table 5

Orientation relationship between an α -Fe substrate and magnetite layer as well as a magnetite substrate and a hematite layer, from [61].

α -Fe	Magnetite	Hematite
$\{001\}\langle 010 \rangle$	$\{001\}\langle 110 \rangle$	$\{114\}$
$\{011\}\langle 100 \rangle$	$\{111\}\langle 110 \rangle$	$\{001\}\langle 100 \rangle$
$\{111\}\langle 011 \rangle$	$\{210\}\langle 100 \rangle$	$\{211\}$

is of great importance. However, also the vacancies present in the oxidation product play a crucial role [66].

The oxidation of polycrystalline Fe-Cr reveals a clear distinction between $\{100\}$, which is less oxidized, and $\{111\}$ & $\{110\}$ crystal planes, as shown in Fig. 1. For the initial oxidation of an Fe_{bcc} substrate, as summarized in [21], the adsorption of oxygen at room temperature results in faster oxidation on the more open $\text{Fe}\{111\}$ surface. When oxidation proceeds, ordered phases on $\text{Fe}\{100\}$ and $\text{Fe}\{110\}$ are formed [21]. However, for unknown reasons the presence of Cr seems to cause an ordered oxide on $\text{Fe-Cr}\{100\}$ and not on $\text{Fe-Cr}\{101\}$ [63].

The initial oxidation in our polycrystalline material at a temperature below 400 °C seems a steady diffusion of cations through the spinel/magnetite layer, as schematically shown in Fig. 8. Oxidation seems to be controlled by bulk diffusion. Because, if transport of ions would occur predominantly along the grain boundaries, a thicker oxide on the grain boundaries would be present. Also lateral growth of the oxide from the boundaries on the grains would take place: a phenomenon which is not observed in Fig. 1. On the contrary, the individual grains possess a very uniform colour contrast and brightness, an indication of a uniform oxide layer. A process which is changing when the temperature is increased towards 450 °C: a non-regular grain decoration is started to be seen, with possible iron oxide substructures, not corresponding to grain boundaries.

On the base of the above presented results and discussion we propose the following physical picture. At temperatures above 200 °C the diffusion speed of cations is promoted. Fe is diffusing faster through the non-structured magnetite layer on $\text{Fe-Cr}\{101\}$ and $\text{Fe-Cr}\{111\}$ compared to more difficult traveling through ordered structures on $\text{Fe-Cr}\{100\}$.

It could be argued that the systems on single crystals studied in literature may apply to describe the system of a polycrystalline alloy. Surprisingly the polycrystalline structure oxidized in a uniform way per grain orientation, where for the first oxidation stage the oxide growth direction was normal to the surface. This allowed for a multi “single crystal” approach where results obtained for single crystals in literature

Fig. 8. Schematic representation of the growth of the oxide layer on Fe-Cr steel. Left: passive layer in the order of several nanometres prior to heat treatment. Right: iron cation diffusion and increasing oxide thickness towards tenths of nanometres during a heat treatment in air.

contributed to the understanding of the oxide structure per grain. It is observed that due to the alloying with Cr, the ORs between the substrate and magnetite are not identical compared to a system with a pure iron substrate. It is, however, the addition of Cr which is beneficial to the corrosion resistance by suppression of ion diffusion. Since the start of this process by Faraday, Stodart and Bertier almost 200 years ago, research on this topic expanded from a pure chemical approach to an approach where the material crystallography is central. Considering experimental conditions representing industrial conditions, this paper is aimed to the understanding of bulk processes on nano- and micro level, hence bridging the gap between metallurgy, microstructural analysis and the onset of corrosion.

5. Conclusions

The major conclusions are the following:

There is a grain direction-oxidation relationship for polycrystalline Fe-Cr steel. The driving factor is the diffusion constant, which is influenced by temperature. The different oxidation processes change gradually whereby the first stage is mainly present up to 350 °C, second stage is most pronounced at 450 °C.

- At the start of oxidation the surface oxidation is decomposed in {001} lacking behind and {111} & {101} planes: {001} < {111} & {101}.
- The second stage of oxidation is split into a threefold system with {001} planes still lacking behind but {101} progress faster than {111}: {001} < {111} < {101}.

The oxide layer consists of a crystalline magnetite inner, and hematite outer sublayers.

The order of oxidation velocity, i.e. {001} < {111} & {101}, has not been reported in literature. In fact for an Fe based system, {001} is found to have the relative highest oxidation velocities, as opposed to results of this work for an Fe-Cr alloy.

Acknowledgements

Thanks are due to Karel Trojan and Jiří Čapek from the Czech Technical University in Prague, for their contribution to the X-ray diffraction analysis. The authors are grateful to Professor Herman Terryn (Free Un. Brussels) for his valuable comments and suggestions. This research was carried out under the project number T63.3.12480 in the framework of the research program of the Materials Innovation Institute, Delft, the Netherlands.

References

- [1] J. Stodart, M. Faraday, Experiments on the alloys of steel made with a view to its improvement, *Philos. Mag. (Ser. 1)* 56 (1820) 26–35, <https://doi.org/10.1080/14786442008652361>.
- [2] P. Berthier, Sur les Alliages du chrome avec le fer et avec l'acier, *Ann. Chim. Phys.* XVII (1821) 55–64.
- [3] J. Stodart, M. Faraday, On the alloys of steel, *Philos. Trans. R. Soc. Lond.* 112 (1822) 253–270.
- [4] P. Monnartz, Beitrag zum Studium der Eisen-Chromlegierungen unter besonderer Berücksichtigung der Säurebeständigkeit (The study of iron-chromium alloys with special consideration of resistance to acids), *Metallurgie* 8 (1911) 161–176.
- [5] G. Zijlstra, M. Groen, J. Post, V. Ocelik, J.T.M. De Hosson, On the role of the residual stress state in product manufacturing, *Mater. Des.* 105 (2016) 375–380, <https://doi.org/10.1016/j.matdes.2016.05.085>.
- [6] S.-Y. Lu, K.-F. Yao, Y.-B. Chen, M.-H. Wang, X.-Y. Ge, Influence of heat treatment on the microstructure and corrosion resistance of 13 Wt Pct Cr-type martensitic stainless steel, *Metall. Mater. Trans. A* 46 (2015) 6090–6102, <https://doi.org/10.1007/s11661-015-3180-1>.
- [7] S.-Y. Lu, K.-F. Yao, Y.-B. Chen, M.-H. Wang, N. Chen, X.-Y. Ge, Effect of quenching and partitioning on the microstructure evolution and electrochemical properties of a martensitic stainless steel, *Corros. Sci.* 103 (2015) 95–104, <https://doi.org/10.1016/j.corsci.2015.11.010>.
- [8] S.-Y. Lu, K.-F. Yao, Y.-B. Chen, M.-H. Wang, X. Liu, X. Ge, The effect of tempering temperature on the microstructure and electrochemical properties of a 13 wt.% Cr-type martensitic stainless steel, *Electrochim. Acta* 165 (2015) 45–55, <https://doi.org/10.1016/j.electacta.2015.02.038>.
- [9] B. Pujilaksono, T. Jonsson, H. Heidari, M. Halvarsson, J.-E. Svensson, L.-G. Johansson, Oxidation of binary FeCr alloys (Fe-2.25Cr, Fe-10Cr, Fe-18Cr and Fe-25Cr) in O₂ and in O₂ + H₂O environment at 600 °C, *Oxid. Met.* 75 (2011) 183–207, <https://doi.org/10.1007/s11085-010-9229-z>.
- [10] T. Jonsson, B. Pujilaksono, H. Heidari, F. Liu, J.-E. Svensson, M. Halvarsson, L.-G. Johansson, Oxidation of Fe-10Cr in O₂ and in O₂ + H₂O environment at 600 °C: a microstructural investigation, *Corros. Sci.* 75 (2013) 326–336, <https://doi.org/10.1016/j.corsci.2013.06.016>.
- [11] T. Jonsson, S. Karlsson, H. Hooshyar, M. Sattari, J. Liske, J.-E. Svensson, L.-G. Johansson, Oxidation after breakdown of the chromium-rich scale on stainless steels at high temperature: internal oxidation, *Oxid. Met.* 85 (2016) 509–536, <https://doi.org/10.1007/s11085-016-9610-7>.
- [12] I. Saeki, T. Saito, R. Furuichi, H. Konno, T. Nakamura, K. Mabuchi, M. Itoh, Growth process of protective oxides formed on type 304 and 430 stainless steels at 1273 K, *Corros. Sci.* 40 (1998) 1295–1305.
- [13] J. Yuan, W. Wang, H. Zhang, L. Zhu, S. Zhu, F. Wang, Investigation into the failure mechanism of chromia scale thermally grown on an austenitic stainless steel in pure steam, *Corros. Sci.* 109 (2016) 36–42, <https://doi.org/10.1016/j.corsci.2016.03.021>.
- [14] D.-I.H. Kim, S.H. Phaniraj, M.P. Han, J.-P.H.N. Ahn, W.Y. Cho, Microstructural analysis of oxide layer formation in ferritic stainless steel interconnects, *Mater. High Temp.* 28 (2011) 285–289, <https://doi.org/10.3184/096034011X13185032513419>.
- [15] C. Juricic, A.H. Pinto, A.D. Cardinali, A.M. Klaus, C. Genzel, A.A.R. Pyzalla, Effect of substrate grain size on the growth, texture and internal stresses of iron oxide scales forming at 450 °C, *Oxid. Met.* 73 (2010) 15–41, <https://doi.org/10.1007/s11085-009-9162-1>.
- [16] C.O.A. Olsson, D. Landolt, Passive films on stainless steels – chemistry, structure and growth, *Electrochim. Acta* 48 (2003) 1093–1104, [https://doi.org/10.1016/S0013-4686\(02\)00841-1](https://doi.org/10.1016/S0013-4686(02)00841-1).
- [17] I. Olefjord, H. Fischmeister, ESCA studies of the composition profile of low temperature oxide formed on chromium steels-II. Corrosion in oxygenated water, *Corros. Sci.* 15 (1975) 697–707, [https://doi.org/10.1016/0010-938X\(75\)90034-7](https://doi.org/10.1016/0010-938X(75)90034-7).
- [18] S. Jin, A. Atrens, Passive films on stainless steels in aqueous media, *Appl. Phys. A* 50 (1990) 287–300, <https://doi.org/10.1007/BF00324495>.
- [19] D. Ramachandran, R. Egoavil, A. Crabbe, T. Hauffman, A. Abakumov, J. Verbeeck, I. Vandendael, H. Terryn, D. Schryvers, TEM and AES investigations of the natural surface nano-oxide layer of an AISI 316L stainless steel microfiber, *J. Microsc.* 264 (2016) 207–214, <https://doi.org/10.1111/jmi.12434>.
- [20] W. Weiss, W. Ranke, Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers, *Prog. Surf. Sci.* 70 (2002) 1–151, [https://doi.org/10.1016/S0079-6816\(01\)00056-9](https://doi.org/10.1016/S0079-6816(01)00056-9).
- [21] G.S. Parkinson, Iron oxide surfaces, *Surf. Sci. Rep.* (2016) 272–365, <https://doi.org/10.1016/j.surfrep.2016.02.001>.
- [22] R. Dieckmann, Point defects and transport in non-stoichiometric oxides: solved and unsolved problems, *J. Phys. Chem. Solids* 59 (1998) 507–525, [https://doi.org/10.1016/S0022-3697\(97\)00205-9](https://doi.org/10.1016/S0022-3697(97)00205-9).
- [23] F. Qin, N.P. Magtoto, M. Garza, J.A. Kelber, Oxide film growth on Fe(111) and scanning tunneling microscopy induced high electric field stress in Fe₂O₃/Fe(111), *Thin Solid Films* 444 (2003) 179–188, <https://doi.org/10.1016/j.tsf.2003.08.043>.
- [24] T. Ossowski, A. Kiejna, Oxygen adsorption on Fe(110) surface revisited, *Surf. Sci.* 637–638 (2015) 35–41, <https://doi.org/10.1016/j.susc.2015.03.001>.
- [25] S. Ekellund, C. Leygraf, A LEED-AES study of the oxidation of Cr(110) and Cr(100), *Surf. Sci.* 40 (1973) 179–199.
- [26] P. Michel, C. Jardin, Oxygen adsorption and oxide formation on Cr(100) and Cr(110) surfaces, *Surf. Sci.* 36 (1973) 478–487, [https://doi.org/10.1016/0039-6028\(73\)90396-8](https://doi.org/10.1016/0039-6028(73)90396-8).
- [27] G. Gewinner, J.C. Peruchetti, A. Jaegle, A. Kalt, Photoemission study of the chromium(111) surface interacting with oxygen, *Surf. Sci.* 78 (1978) 439–458, [https://doi.org/10.1016/0039-6028\(78\)90090-0](https://doi.org/10.1016/0039-6028(78)90090-0).
- [28] V. Maurice, S. Cadot, P. Marcus, XPS, LEED and STM study of thin oxide films formed on Cr(110), *Surf. Sci.* 458 (2000) 195–215.
- [29] J.R. Lince, S.V. Didziulis, D.K. Shuh, T.D. Durbin, J.A. Yarmoof, Interaction of O₂ with the Fe_{0.84}Cr_{0.16}(001) surface studied by photoelectron spectroscopy, *Surf. Sci.* 277 (1992) 43–63, [https://doi.org/10.1016/0039-6028\(92\)90611-9](https://doi.org/10.1016/0039-6028(92)90611-9).
- [30] H. Fujiyoshi, T. Matsui, J. Yuhara, Segregation and morphology on the surface of ferritic stainless steel (001), *Appl. Surf. Sci.* 258 (2012) 7664–7667, <https://doi.org/10.1016/j.apsusc.2012.04.116>.
- [31] F. Genuzio, A. Sala, T. Schmidt, D. Menzel, H.-J. Freund, Interconversion of α -Fe₂O₃ and Fe₃O₄ Thin films: mechanisms, morphology, and evidence for unexpected substrate participation, *J. Phys. Chem. C* 118 (2014) 29068–29076, <https://doi.org/10.1021/jp504020a>.
- [32] F. Genuzio, A. Sala, T. Schmidt, D. Menzel, H.J. Freund, Phase transformations in thin iron oxide films: spectromicroscopic study of velocity and shape of the reaction fronts, *Surf. Sci.* 648 (2016) 177–187, <https://doi.org/10.1016/j.susc.2015.11.016>.
- [33] N. Cabrera, N.F. Mott, Theory of the oxidation of metals, *Reports Prog. Phys.* 12 (1949) 163–184, <https://doi.org/10.1088/0034-4885/12/1/308>.
- [34] K.R. Lawless, The oxidation of metals, *Rep. Prog. Phys.* 37 (1974) 231–316, <https://doi.org/10.1149/1.3071795>.
- [35] A. Atkinson, Transport processes during the growth of oxide films at elevated temperature, *Rev. Mod. Phys.* 57 (1985) 437–470.
- [36] K. Fushimi, A. Kazuhisa, M. Seo, Evaluation of heterogeneity in thickness of passive iron by scanning electrochemical microscopy films on pure, *ISIJ Int.* 39 (1999) 346–351.

- [37] A. Schreiber, C. Rosenkranz, M.M. Lohrengel, Grain-dependent anodic dissolution of iron, *Electrochim. Acta* 52 (2007) 7738–7745, <https://doi.org/10.1016/j.electacta.2006.12.062>.
- [38] K. Fushimi, Y. Takabatake, T. Nakanishi, Y. Hasegawa, Microelectrode techniques for corrosion research of iron, *Electrochim. Acta* 113 (2013) 741–747, <https://doi.org/10.1016/j.electacta.2013.03.021>.
- [39] J. Kunze, V. Maurice, L.H. Klein, H.H. Strehblow, P. Marcus, In situ STM study of the duplex passive films formed on Cu(111) and Cu(001) in 0.1 M NaOH, *Corros. Sci.* 46 (2004) 245–264, [https://doi.org/10.1016/S0010-938X\(03\)00140-9](https://doi.org/10.1016/S0010-938X(03)00140-9).
- [40] L. Lapeire, E. Martinez Lombardia, K. Verbeken, I. De Graeve, L.A.I. Kestens, H. Terryn, Effect of neighboring grains on the microscopic corrosion behavior of a grain in polycrystalline copper, *Corros. Sci.* 67 (2013) 179–183, <https://doi.org/10.1016/j.corsci.2012.10.017>.
- [41] E. Martinez-Lombardia, Y. Gonzalez-Garcia, L. Lapeire, I. De Graeve, K. Verbeken, L. Kestens, J.M.C. Mol, H. Terryn, Scanning electrochemical microscopy to study the effect of crystallographic orientation on the electrochemical activity of pure copper, *Electrochim. Acta* 116 (2014) 89–96, <https://doi.org/10.1016/j.electacta.2013.11.048>.
- [42] J.R. Davis, *ASM Specialty Handbook: Stainless Steels*, 1994.
- [43] W.H.J. Vernon, E.A. Calnan, C.J.B. Clews, T.J. Nurse, The oxidation of iron around 200 degrees C, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 216 (1953) 375–397, <https://doi.org/10.1098/rspa.1953.0028>.
- [44] U.R. Evans, The colours due to thin films on metals, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 107 (1925) 228–237.
- [45] W.H.J. Vernon, F. Wormwell, T.J. Nurse, The thickness of air-formed oxide films on iron, *J. Chem. Soc.* 624–632 (1939).
- [46] R.L. Higginson, C.P. Jackson, E.L. Murrell, P.A.Z. Exworthy, R.J. Mortimer, D.R. Worrall, G.D. Wilcox, Effect of thermally grown oxides on colour development of stainless steel, *Mater. High Temp.* 32 (2015) 113–118, <https://doi.org/10.1179/0960340914Z.00000000083>.
- [47] F.H. Constable, Spectroscopic observations on the growth of oxide films on Iron, Nickel, and Copper, *Proc. Roy. Soc.* 117 (1928) 376–387.
- [48] T. Fujii, F.M.F. De Groot, G.A. Sawatzky, F.C. Voogt, T. Hibma, K. Okada, In situ XPS analysis of various iron oxide films grown by NO₂-assisted molecular-beam epitaxy, *Phys. Rev. B* 59 (1999).
- [49] T. Yamashita, P. Hayes, Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials, *Appl. Surf. Sci.* 254 (2008) 2441–2449, <https://doi.org/10.1016/j.apsusc.2007.09.063>.
- [50] S. Suzuki, K. Sugiyama, Y. Waseda, Changes in the chemical state and composition of the surface of iron oxides due to argon ion sputtering, *J. Surf. Anal.* 9 (2002) 455–458.
- [51] E.J.W. Verwey, E.L. Heilmann, Physical properties and cation arrangement of oxides with spinel structures I, *J. Chem. Phys.* 15 (1947) 1091–1120, <https://doi.org/10.1063/1.1747852>.
- [52] E.J. Verwey, P.W. Haayman, F.C. Romeijn, Physical properties and cation arrangement of oxides with spinel structures II, *J. Chem. Phys.* 15 (1947) 181–187, <https://doi.org/10.1063/1.1746466>.
- [53] H.J. Yearian, J.M. Kortright, R.H. Langenheim, Lattice parameters of the FeFe (2-x)Cr_xO₄ spinel system, *J. Chem. Phys.* 22 (1954) 1196–1197, <https://doi.org/10.1063/1.1740331>.
- [54] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.* 257 (2010) 2717–2730, <https://doi.org/10.1016/j.apsusc.2010.10.051>.
- [55] J. Landoulsi, M.J. Genet, S. Fleith, Y. Touré, I. Liascukienė, C. Méthivier, P.G. Rouxhet, Organic adlayer on inorganic materials: XPS analysis selectivity to cope with adventitious contamination, *Appl. Surf. Sci.* 383 (2016) 71–83, <https://doi.org/10.1016/j.apsusc.2016.04.147>.
- [56] R. Steinberger, C.E. Celedón, B. Bruckner, D. Roth, J. Duchoslav, M. Arndt, P. Kürsteiner, T. Steck, J. Faderl, C.K. Riemer, G. Angeli, P. Bauer, D. Stifter, Oxygen accumulation on metal surfaces investigated by XPS, AES and LEIS, an issue for sputter depth profiling under UHV conditions, *Appl. Surf. Sci.* 411 (2017) 189–196, <https://doi.org/10.1016/j.apsusc.2017.03.163>.
- [57] Y. Zhou, J. Xuesong, Y.M. Mukovskii, I.V. Shvets, Kinetics of oxidation of low-index surfaces of magnetite, *J. Phys. Condens. Matter.* 16 (2004) 1–12, <https://doi.org/10.1088/0953-8984/16/1/001>.
- [58] K.W. Raine, P.N. Quedsted, Interference film microscopy for metal phase identification, *Microsc. Capab.* 368 (1982) 110–118.
- [59] B. Pöter, I. Parezanović, M. Spiegel, In-situ scanning electron microscopy and electron backscatter diffraction investigation on the oxidation of pure iron, *Mater. High Temp.* 22 (2005) 185–193, <https://doi.org/10.1179/mht.2005.021>.
- [60] J.B. Wagner, K.R. Lawless, A.T. Gwathney, Rate of formation and structure of oxide films formed on single crystal of iron, *Trans. Met. Soc. AIME* 221 (1961) 257–261.
- [61] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Users*, second ed., WILEY-VCH, 2003.
- [62] M. Gebhardt, *Epitaxy in Crystal Growth: An Introduction*, North-Holland Publishing Co, 1973.
- [63] C. Leygraf, G. Hultquist, S. Ekelund, A LEED/AES study of the oxidation of Fe_{0.84}Cr_{0.16} (100) and (110), *Surf. Sci.* 51 (1975) 409–432, [https://doi.org/10.1016/0039-6028\(75\)90391-X](https://doi.org/10.1016/0039-6028(75)90391-X).
- [64] F.A. Kröger, H.J. Vink, Relations between the concentrations of Imperfections in crystalline, Solids, *Solid State Phys. Adv. Res. Appl.* 3 (1956) 307–435, [https://doi.org/10.1016/S0081-1947\(08\)60135-6](https://doi.org/10.1016/S0081-1947(08)60135-6).
- [65] N.F. Mott, Materials with mixed valency that show a verwey transition, *Philos. Mag. B Phys. Condens. Matter; Stat. Mech. Electron. Opt. Magn. Prop.* 42 (1980) 327–335, <https://doi.org/10.1080/01418638008221874>.
- [66] S. Hallström, L. Höglund, J. Ågren, Modeling of iron diffusion in the iron oxides magnetite and hematite with variable stoichiometry, *Acta Mater.* 59 (2011) 53–60, <https://doi.org/10.1016/j.actamat.2010.08.032>.