Oxidation mechanism of nickel particles studied in an environmental transmission electron microscope

Q. Jeangros\textsuperscript{a,*}, T.W. Hansen\textsuperscript{b}, J.B. Wagner\textsuperscript{b}, R.E. Dunin-Borkowski\textsuperscript{c}, C. Hébert\textsuperscript{a}, J. Van herle\textsuperscript{d}, A. Hessler-Wyser\textsuperscript{a}

\textsuperscript{a} Interdisciplinary Centre for Electron Microscopy, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
\textsuperscript{b} Center for Electron Nanoscopy, Technical University of Denmark, Kgs. Lyngby, Denmark
\textsuperscript{c} Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Jülich Research Centre, Jülich, Germany
\textsuperscript{d} Fuelmat Group, Faculty of Engineering Sciences and Technology STI, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

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Abstract

The oxidation of nickel particles was studied in situ in an environmental transmission electron microscope in 3.2 mbar of O\textsubscript{2} between ambient temperature and 600 °C. Several different transmission electron microscopy imaging techniques, electron diffraction and electron energy-loss spectroscopy were used to study the evolution of the microstructure and the local chemical composition of the particles during oxidation. Our results suggest that built-in field effects control the initial stages of oxidation, with randomly oriented NiO crystallites and internal voids then forming as a result of outward diffusion of Ni\textsuperscript{2+} along NiO grain boundaries, self-diffusion of Ni\textsuperscript{2+} ions and vacancies, growth of NiO grains and nucleation of voids at Ni/NiO interfaces. We also observed the formation of transverse cracks in a growing NiO film in situ in the electron microscope.

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1. Introduction

The reaction of nickel with oxygen is important for a variety of applications, including solid oxide fuel cells. There, the Ni anode catalyst, which is typically present on the fuel side in the form of sub-micron-sized grains that are co-sintered with a ceramic material, may oxidize if the gas environment deviates from reducing working conditions, resulting in failure of the device \cite{1,2}. The oxidation mechanism that controls the final microstructure is complex, with neither of the two primary models for ionic and electronic transport across oxide films being directly applicable under these conditions \cite{3}. The first model is denoted the Mott–Cabrera theory and describes non-linear growth of a thin oxide film \cite{4} (below \textasciitilde 10 nm for NiO \cite{3}), across which electrons tunnel from the metal to ionize adsorbed oxygen, resulting in a large electric field that drives ion transport and oxide growth. The second model, denoted the Wagner theory, applies to oxide films that are in local chemical equilibrium and significantly thicker \cite{5} (above \textasciitilde 1 \textmu m for NiO at 500 °C \cite{3}). This description assumes that oxide growth is controlled by ion diffusion in a gradient of oxygen chemical potential, resulting in a parabolic growth rate. The growth of a thick NiO film on Ni at high temperature (>1000 °C) follows this behaviour, with diffusion of Ni\textsuperscript{2+} through the NiO lattice controlling the growth rate. At lower temperatures, Ni\textsuperscript{2+} diffusion through the oxide grain boundaries must be included in the description \cite{6} and, as the number of these fast-diffusion paths evolves as a function of time and temperature, the growth rate deviates from a purely parabolic behaviour \cite{7}.

The microstructure that forms during Ni oxidation is closely related to the growth-controlling mechanism.
Inward diffusion of O\(^{2-}\) has been measured to be several orders of magnitude slower than outward diffusion of Ni\(^{2+}\), suggesting that Ni vacancies are injected at Ni/NiO interfaces [8]. If the vacancies cannot be annihilated (e.g., by dislocations or interface recession), then internal porosity that is similar in size to each initial Ni particle can form [9]. Recent studies have made use of this interface phenomenon (also referred to as a nano-Kirkendall effect, even though Ni\(^{2+}\) and O\(^{2-}\) transport occur at different crystallographic locations) to form core (void)–shell (NiO) structures by the oxidation of Ni nanoparticles [10–13]. NiO films that have thicknesses of a few \(\mu\)m and are formed by oxidation below 1000 °C can have duplex structures, with additional NiO growth occurring inwards (at the metal/oxide interface). Microchannels in NiO scales are thought to act as paths for the inward permeation of O\(_2\) towards unreacted Ni [7,14–17].

As it is difficult to relate microstructural changes to reaction-controlling mechanisms solely on the basis of post-exposure examinations, attempts have been made to study Ni oxidation in situ across different length scales using techniques that include transmission electron microscopy (TEM) [18–20], environmental scanning electron microscopy [21,22] and full-field transmission X-ray microscopy [23]. Although different stages of oxidation have been described, such as NiO nucleation on Ni and the formation of characteristic NiO microstructural features, they have not been followed in detail or related to rate-controlling mechanisms from the formation of the first nm of oxide to completion of the reaction.

Environmental TEM (ETEM) can be used to record high spatial resolution images of microstructure and chemistry in an electron-transparent specimen held in a gas environment at elevated temperature [24]. The oxidation of Ni nanoparticles (with sizes of <30 nm) has been studied in an ETEM by Rez et al. [25], who measured changes in oxidation state as a function of temperature using electron energy-loss spectroscopy (EELS), as well as by Chenna et al. [26], who observed NiO shell structures after oxidation as a result of diffusion mechanisms. Here, we use a methodology that we introduced previously [27] to provide detailed measurements of the temperature-dependent relationship between the structural and chemical evolution of NiO, the oxide growth rate and the reaction-controlling mechanism on the nanometre scale, including local and transient considerations.

2. Experimental details

2.1. Materials

NiO powder was obtained from JT Baker\textsuperscript{™} (NiO > 99.0 wt.% with Co, Fe, Pb, Si, Na, S and Zn as the main impurities) [27]. The smallest primary particles were measured to be \(\sim 50\) nm using optical diffraction, with an average agglomerate size of \(\sim 990\) nm, while the average crystallite size was measured to be \(\sim 100\) nm using X-ray diffraction. NiO was chosen as the starting material, rather than Ni, in order to take the specimen through one complete reduction–oxidation cycle using ETEM.

2.2. Electron microscopy

NiO particles were dispersed onto Au grids covered with holey silicon oxide films (Au–SiO) and examined at 300 kV using a Gatan Inconel 652 double-tilt heating holder in an FEI Titan environmental transmission electron microscope, in which a differential pumping system allows the introduction of a selected mixture of gases around the specimen [28]. Prior to oxidation, each NiO specimen was reduced to Ni inside the microscope in 1.3 mbar of H\(_2\) at 600 °C for 210 min [27]. The specimen was then cooled to room temperature, before the H\(_2\) gas was pumped out of the environmental cell (see Fig. 1). A flow rate of 2 m\(l\)\(_N\) min\(^{-1}\) of O\(_2\) was then introduced, corresponding to a pressure of 3.2 mbar. Oxidation of the Ni particles was investigated in situ in the electron microscope using conventional bright-field (BF) and dark-field (DF) imaging, high-resolution TEM (HRTEM), selected area electron diffraction (SAED), high-angle annular DF (HAADF) scanning TEM (STEM) and EELS.

2.2.1. Heating sequences to probe the oxidation kinetics and resulting structural changes

During oxidation, each region of interest was characterized after chosen time intervals by recording conventional TEM images, SAED patterns and core-loss EEL spectra (in diffraction mode using an acquisition time of 60–120 s and an energy range of 500–900 eV). Three different temperature ramps were followed, each using a different sample, to achieve three different heating rates (Fig. 1). The starting temperature for each ramp was 250 °C, as the oxidation kinetics was negligible at lower temperatures [29]. The temperature was kept constant for 5 min at each step while TEM images, SAED patterns and EEL spectra were recorded. A separate set of measurements (involving the acquisition of an image, a diffraction pattern and an EEL spectrum) was performed at each step in each ramp.

Fig. 1. Time and temperature parameters used to reduce the NiO particles isothermally and then to re-oxidize the resulting Ni particles to NiO, while ramping the temperature at equivalent average rates of 2, 4 or 6 K min\(^{-1}\). A separate set of measurements (involving the acquisition of an image, a diffraction pattern and an EEL spectrum) was performed at each step in each ramp.
acquired, before increasing the temperature by 12, 24 or 36 K over 1–2 min to achieve overall heating rates of 2, 4 or 6 K min\(^{-1}\), respectively, up to a maximum temperature of 600 °C. This approach minimized the influence of thermal drift of the holder and the grid on the measurements. The uncertainty in the sample temperature was estimated to be \(\sim 10\) K. An electron dose rate of \(\sim 800\) e\(^{-}\) nm\(^{-2}\) s\(^{-1}\) was chosen as a compromise between beam damage and EELS signal. Each specimen was irradiated continuously during each experiment.

2.2.2. In situ HRTEM, BF TEM and STEM

HRTEM images (showing lattice fringes) were initially acquired before the introduction of O\(_2\) gas into the microscope column to study the nucleation of NiO on Ni, as Ni is predicted thermodynamically to oxidize at room temperature when H\(_2\) is removed from the microscope column and the pressure reaches \(\sim 10^{-6}\) mbar (the partial pressure of O\(_2\) is then \(\sim 10^{-7}\) mbar) [30]. After the introduction of 3.2 mbar of O\(_2\), BF TEM micrographs were recorded every 100 K between room temperature and 600 °C and STEM HAADF images were recorded at 300 °C. Regions that had not been irradiated using the electron beam were also characterized and compared to areas that had been studied previously to assess electron-beam-induced artefacts.

2.3. Ni oxidation kinetics from electron energy-loss spectroscopy

EEL spectra acquired during the heating experiments were used to infer the reaction kinetics using a procedure that is described in detail elsewhere [27] and makes use of the dependence of the shape of the Ni L\(_{2,3}\) ionization edge and in particular the ratio between the intensities of the L\(_2\) and L\(_3\) white lines on the degree of oxidation [31,32]. Each spectrum contained the O K edge (532 eV), which is dominated by contributions from the SiO support and O\(_2\) gas, and the Ni(O) white lines (L\(_{3}\) at 855 eV and L\(_2\) at 872 eV). All of the spectra were aligned by cross-correlation, meaning that the change in the position of the L\(_3\) edge by \(-0.2\) eV between Ni and NiO was not followed in the present study [31]. Noise was reduced using principal component analysis (the first eight components were selected) [33] and background subtraction was performed using a power law fitted over an energy range of 50 eV before the L\(_3\) edge.

The three sets of EEL spectra acquired at heating rates of 2, 4 and 6 K min\(^{-1}\) exhibited slight differences in energy resolution due to variations in post-column filter tuning. In order to ensure comparable results, each set of spectra was convoluted with an artificial point spread function, which was chosen so that the initial NiO spectra of each set/sample (acquired before reduction) had the same energy resolution (full width at half maximum) at the position of the L\(_3\) edge. NiO and Ni reference spectra were acquired from a similar specimen (with the same NiO particles dispersed on a Au–SiO film), either at room temperature for NiO or at 700 °C for Ni after full reduction in 1.3 mbar of H\(_2\) (the full reaction was confirmed by diffraction). The shape of the L\(_3\) and L\(_2\) edge in each spectrum was fitted using either polynomial functions or a sum of Lorentzian and Gaussian functions. The fitted functions were then integrated using 4 eV windows centred on their maxima. \(I(L_3)/I(L_2)\) ratios were measured from the spectra that had been acquired during oxidation and normalized using the reference spectra to obtain the fraction of NiO in the observed area. The NiO and Ni reference spectra were also fitted directly to each experimental spectrum using a multi-ple linear least squares (MLLS) method [25]. By using these approaches, the total amount of NiO and thus the degree of conversion of the oxidation reaction \(x\) could be measured as a function of temperature.

For a linear heating rate experiment, the rate of a single step solid-state reaction \(dz/dT\) is usually described using an Arrhenius function multiplied by a reaction model function \(f(x)\) using the expression [34]

\[
\frac{dz}{dT} = \frac{A}{\beta} e^{-(E_a/RT)} f(x),
\]

(1)

where \(\beta = dT/dt \) (K s\(^{-1}\)) is the heating rate, \(E_a\) (J mol\(^{-1}\)) is the activation energy, \(A\) (s\(^{-1}\)) is a pre-exponential factor and \(R\) is the universal gas constant. By separating the variables, the temperature integral can be replaced by a third rational approximation (with \(x = E_a/RT\)) in the form [35]

\[
g(x) \approx \frac{A}{\beta} R \left[ e^{-x} \frac{x^2 + 10x + 18}{x^3 + 12x^2 + 36x + 24} \right]^{x}. \tag{2}
\]

The integral solid-state reaction model \(g(x)\) describes how a solid reactant (Ni) is transformed into a solid product (NiO). As \(E_a\) and \(A\) do not depend on heating rate, \(x–T\)

Fig. 2. NiO nucleation on Ni observed at room temperature in the ETEM at an O\(_2\) partial pressure of \(10^{-7}\) mbar. (a) HRTEM image showing the nucleation stage of NiO and (b) its FFT. (c) Inverse FFT (pseudo-DF) image generated from Ni 200 reflections (red), with the HRTEM image added as a background. (d) Inverse FFT images corresponding to NiO 111, 200 and 220 reflections (magenta, blue and green, respectively), with the HRTEM image added as a background. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
profiles obtained for heating rates of 2, 4 and 6 K min$^{-1}$ were fitted simultaneously to obtain values of $E_a$ and $A$ for a specific reaction model using a least squares minimization algorithm. The aim of this procedure was to infer the mechanism that controls the oxidation of the Ni particles. The mechanism could then be interpreted with reference to the observed structural changes.

3. Experimental results

3.1. Ni structural evolution during in situ oxidation

After the NiO particles had undergone reduction at 600 °C for 210 min in 1.3 mbar of H$_2$, the surface of the metallic Ni particles was allowed to oxidize in the microscope at room temperature in a pressure of 10$^{-6}$ mbar, as shown in Fig. 2. A stable 3–4 nm film of NiO was observed to form on their surfaces.

3.2 mbar of O$_2$ was then introduced into the microscope. Fig. 3 shows a selection of TEM images and diffraction patterns illustrating the changes that occur during the 4 K min$^{-1}$ ramp. Fig. 3a shows the initial microstructure. Faint NiO reflections with specific orientations can be observed in the diffraction pattern (see also Supplementary Fig. S.1). The microstructure is not affected noticeably as the temperature is raised to 250 °C (to the start of the temperature ramp; Fig. 3b). At 321 °C (Fig. 3c), weak NiO reflections with random orientations become visible in the diffraction pattern, even though no clear changes can be identified in the images. At 417 °C (Fig. 3d), the particle surfaces become irregular (see inset) and rings in the diffraction patterns from NiO domains become clearly visible. The insets labelled d$'$ show recession of the internal surface (the Ni core) and expansion of the NiO shell between 345 and 467 °C. Fig. 3e (514 °C) corresponds to a nearly fully oxidized state, when the particles have

![Fig. 3. BF TEM images and diffraction patterns acquired in the ETEM in 3.2 mbar of O$_2$ during Ni oxidation. (a) The structure at room temperature soon after introducing O$_2$. (b–f) The structural changes that occur when the specimen is heated at 4 K min$^{-1}$. Insets labelled d$'$ illustrate changes that occur between 345 and 467 °C. Arrows highlight contraction of the Ni.](image-url)
expanded significantly and their contrast is irregular due to the presence of crystallites (and voids). The end of the heating ramp is reached at 608°C (Fig. 3f). All of the reflections in the diffraction patterns acquired during the ramps can be indexed as either Ni or NiO (with reference to simulations performed using JEMS software [36]; see also Supplementary Fig. S.1).

STEM HAADF images, which are sensitive to mass-thickness contrast, were acquired at 300°C in 3.2 mbar of O₂ (Fig. 4). A line profile shown in Fig. 4a exhibits a drop in intensity at the interface between NiO and Ni, suggesting the presence of voids and a loss of contact between the two materials. Adjustment of the contrast in the image can be used to highlight the voids, as shown in Fig. 4c. The NiO film also appears to be ruptured in some regions (see circles in Fig. 4a and c).

Changes in diffraction contrast in BF TEM images can be used to provide information about the evolution of the Ni(O) grain size during oxidation (Fig. 5). While the particles initially consist of large Ni crystallographic domains (~100 nm in size in Fig. 5a), NiO domains below 50 nm in size are observed at 600°C after oxidation (Fig. 5b). A double-layer structure observed after oxidation (ellipse in Fig. 5b) may have resulted from fracturing of the outer NiO, allowing inward permeation of O₂ and the formation of NiO directly at the Ni/NiO interface.

Fig. 5b shows that the NiO particles exhibit irregular contrast at 600°C, as they are made up of randomly oriented crystallites (see the diffraction pattern in Fig. 3f) and voids. As a result of the latter effect, the projected area of the NiO particles after reduction-oxidation is greater than that of the as-received NiO particles (Fig. 6).

3.2. EELS kinetic analysis

Fig. 7 shows, for the specific case of the 4 K min⁻¹ ramp, how the reaction kinetics were obtained from the
EEL spectra, which were recorded every 6 min, corresponding to one spectrum every 24 K (Fig. 7a). As mentioned above, the reaction kinetics in Fig. 7d were obtained either by fitting each spectrum using a linear combination of NiO and Ni reference spectra (Fig. 7b) or by using the Ni L3/L2 ratio (determined using polynomial or Lorentzian–Gaussian fits and 4 eV integration windows), which was normalized using ratios of intensities measured from the NiO and Ni reference spectra (Fig. 7c). The two techniques yield indistinguishable results. The fraction of NiO at room temperature in the presence of O2 is found to be 0.1 for this sample. This amount cannot be attributed solely to the <5 nm oxide layer that forms after removal of H2 from the ETEM. Some NiO domains are therefore inferred to be present at the beginning of the reaction and to contribute to the total fraction of NiO (see Supplementary Fig. S.2). As these domains do not form during the oxidation process, the fraction x of Ni converted to NiO was chosen to be 0 at the beginning of the reaction (right axis in Fig. 7d). In this way, the 3–4 nm NiO film that forms in high vacuum was neglected. This assumption is justified by the fact that a negligible fraction of the Ni is converted to NiO compared to the particle size (>100 nm).

Fig. 8a shows the reaction kinetics measured for heating rates of 2, 4 and 6 K min\(^{-1}\) by the white lines ratio method (using polynomial fits for integration; the other techniques yield the same results). The measurements show that none of the samples was fully reduced after 210 min at 600 °C in 1.3 mbar of H2, with the unreduced fraction varying from 0.1 to 0.2.

Out of the solid-state kinetic models that were investigated (nucleation, reaction order, geometrical contraction, etc. [34]), only the models that describe the reaction as a diffusion-controlled process yield results that are consistent with the experimental measurements. Although these diffusion models (listed in Refs. [34,37,38]) yield comparable results with similar values of \(E_a\) and \(A\), the phenomenological description of oxidation of spherical particles derived by Niklasson and Karmhag appears to be better suited here [39]. Indeed, it describes the oxidation of nanometre-sized particles and thus includes built-in field effects for the initial stages of the reaction (up to a critical thickness \(L_{cr}\), which is chosen here to be 10 nm, as in Ref. [40]), while the rest of the reaction is described as a linear diffusion process. The model is rewritten in Table 1 as a function of the initial Ni particle diameter \(d_0\) and using the Pilling–Bedworth ratio \(q\) (the volume of product formed per volume of reactant; here 1.65 for NiO/Ni [41]). The value of \(d_0\) can be estimated from the TEM images and knowing the correspondence between \(x\) and \(T\) for a heating
rate $\beta$ (Fig. 8a), $g(x)$ can be integrated numerically for an experimental value of $x$, while the corresponding values of $T$ and $\beta$ are inserted on the right side of Eq. (2). $E_a$ and $A$ can then be estimated using an algorithm that minimizes the least squares differences between the values of $g(x)$ and their corresponding approximation of the temperature integral (Nelder–Mead method [42]). As the particle size is not homogeneous here and is observed to range from ~100 to 400 nm (Fig. 3), these two boundary values are used as separate $d_0$ to infer two different sets of values of $E_a$ and $A$, as lower and upper limits of the kinetic description (Table 1). A rational description for the data is obtained at heating rates of 2 and 4 K min$^{-1}$, while the measurements obtained at 6 K min$^{-1}$ are shifted to lower temperatures when compared to the model (Fig. 8b).

The results of the model fitting procedure ($E_a$ and $A$) can be used to determine the rate constant $k_p$ (in units of cm$^{-2}$ s$^{-1}$), giving the speed of the reaction; see Table 1 as a function of temperature for particle sizes chosen as 100 and 400 nm (Fig. 9). Values obtained for the rate constant from EELS can then be compared to those obtained experimentally in the literature. As the reaction appears to be diffusion-controlled, the values can also be compared to predictions based on diffusion coefficients. For a reaction that is controlled by linear diffusion in an oxide film, which is in local chemical equilibrium, the value of $k_p$ at a certain temperature is related directly to the diffusion coefficient of the ionic species that controls the reaction (Ni$^{2+}$ in the NiO lattice and grain boundaries) [6] in the form

$$k_p = 6.4 \frac{D_{\text{lattice}} + 2(D'\delta)}{g},$$

(3)

where $D_{\text{lattice}}$ is the tracer diffusion coefficient of Ni$^{2+}$ in the NiO lattice (from Ref. [6]: $4.5 \times 10^{-19}$ cm$^2$ s$^{-1}$ at 500 °C and $3.7 \times 10^{-17}$ cm$^2$ s$^{-1}$ at 600 °C in 1.01 bar of O$_2$), $(D'\delta)$ is the tracer grain boundary diffusion coefficient ($7.4 \times 10^{-20}$ cm$^2$ s$^{-1}$ at 500 °C, $1.6 \times 10^{-18}$ cm$^2$ s$^{-1}$ at 600 °C in 1.01 bar of O$_2$) and $g$ is the oxide grain size (estimated from the images to be ~50 nm at the end of the oxidation process; see Fig. 5b). As measurements in the literature were obtained at atmospheric oxygen pressure, comparisons with the EELS data are only qualitative and should take into account the fact that $k_p$ is proportional to $p_{O_2}^{1/4} - p_{O_2}^{1/6}$ [7].

4. Discussion

4.1. Initial stages of the oxidation process

After reduction in H$_2$, the samples are initially exposed to a partial pressure of ~10$^{-7}$ mbar of O$_2$. NiO domains then nucleate with random orientations, impinge and grow to form continuous shells around the particles, which stabilize at a thickness of 3–4 nm (Fig. 2). Similar oxide structures have been observed ex situ by Railsback et al. [12] and Graham and Cohen [45]. In the present study, even though the dynamics of the thin NiO layer growth could not be captured, the behaviour can be related qualitatively to the description of Cabrera and Mott [4]. According to this model, once the NiO domains have impinged to form a continuous layer, oxide growth continues by field-driven transport of Ni$^{2+}$ through the NiO. Over this length scale, electrons can tunnel from the metal across the oxide film to ionize adsorbed oxygen. A large electric field then builds up in the film, driving the transport of Ni$^{2+}$ through the NiO without the need for thermal activation. Once the oxide layer has reached a thickness of 3–4 nm, electron transfer becomes negligible and the oxide growth rate approaches zero. In our experiments, the polycrystalline oxide does not grow further, either at room temperature when O$_2$ is introduced at a pressure of 3.2 mbar or when the temperature is increased to 100 °C (Fig. 5a). Moreover, the reaction rate measured using EELS remains slow up to 250 °C (Fig. 7d).

4.2. Structural evolution of Ni(O) particles until full oxidation

4.2.1. Voids nucleation at the NilNiO interfaces

The contrast in the STEM HAADF image shown in Fig. 4 suggests that at 300 °C voids have already formed.
at the Ni/NiO interface, i.e., that transport of Ni\(^{2+}\) across the NiO film is faster than that of O\(^{2-}\), as expected based on the diffusion coefficients of Ni\(^{2+}\) and O\(^{2-}\) [3]. New NiO domains therefore form outwards at the NiO/O\(_2\) interface, while Ni vacancies are injected at the Ni/NiO interface to balance the outward mass flux. The mobility of these vacancies, which accumulate and coalesce at the interface, results in the nucleation of multiple voids along the Ni/NiO interface [12]. Voids that have sizes of \(~10\) nm are observed in the vicinity of convex Ni regions, while in other regions the pores take the form of thin flat layers that have a thickness below 5 nm. It appears that Ni/NiO contact may be more difficult to maintain in curved than in flat regions, where the interface may recess more easily [46].

4.2.2. Formation of transverse cracks in the NiO film

The NiO film is also observed to break in some regions, creating a temporary permeation channel for gaseous O\(_2\) to a fresh Ni surface [3] (circled regions in Figs. 4a–c and ellipse in \(\pm\)b). New NiO domains can then form directly on the Ni surface, in turn closing the O\(_2\) permeation channel. The oxide growth rate is sufficiently slow at 300 °C (taking at least a few seconds) that this process can be captured in STEM mode. In contrast to other techniques, such as post mortem structural examination or acoustic emission, ETEM has the ability to resolve this process in situ and spatially, allowing the underlying mechanisms to be discussed with regard to geometrical/structural considerations. The same phenomenon has been reported to occur in planar NiO films that have a thickness of above a few \(\mu\)m and to result in the formation of a characteristic duplex microstructure [47]. The oxide fracture observed in the present experiment is located at the edge of an irregular Ni structure and runs through an oxide film of thickness \(~10\) nm. While different models have been proposed to describe the formation of cracks in oxide films [3,41,46], the irregular geometry of the Ni particles investigated here probably results in additional stress in the oxide [48]. While oxide growth stress is usually compressive and would be expected to close any potential crack, inhomogeneities arising from local differences in oxide growth rate, which could be caused by local loss of contact between NiO and Ni (as observed in Fig. 4), may be sufficient to rupture the film locally [49]. Growth of the NiO film near the curved edges is probably hindered, as the supply of Ni\(^{2+}\) through the film is disrupted by the loss of contact between Ni and NiO, resulting in a higher rate of NiO growth in the flatter regions where the Ni/NiO contact area is higher.

4.2.3. Polycrystalline NiO structures with internal voids

At higher temperatures (Fig. 3d–f), the contrast in the images becomes irregular as the NiO film grows, with NiO reflections in diffraction patterns indicating random grain orientations. As shown in Fig. 3d, the internal Ni surface retracts in one direction, maintaining contact with the NiO that covers it in some areas while leaving voids elsewhere. This observation is similar to that of Railsback et al. [12] and requires self-diffusion of Ni along with that of vacancies to maintain contact between Ni and NiO as oxidation continues. The final microstructure contains internal voids and small randomly oriented NiO crystallites of \(<50\) nm in size when the temperature reaches 600 °C (Fig. 3e and f). As a result of internal porosity, the re-oxidized NiO particles now appear significantly larger in projection than before undertaking a reduction–oxidation cycle (Fig. 6). Ni reflections are not detected above 500 °C (Fig. 3 and Supplementary Fig. S1), with EELS results confirming full oxidation at this temperature (Fig. 7d).

4.3. Chemical evolution of Ni(O) particles until full oxidation

4.3.1. Diffusion model describing the oxidation kinetics

Close examination of the structural changes that occur during oxidation provides some information about the mechanisms involved. Further insights can be inferred by assessing the oxidation kinetics. Progress of the reaction with temperature exhibits a similar shape for overall rates of 2, 4 and 6 K min\(^{-1}\) (Fig. 8), indicating that the same mechanism probably controls the reaction in each case. In contrast to theoretical predictions (see Eq. (1)), the curve measured at 6 K min\(^{-1}\) is shifted to lower temperature when compared with the curves obtained at 2 and 4 K min\(^{-1}\). Although the reason behind this observation is unclear, slight differences in the Au grids and SiO films used could introduce a systematic error. Specimen-dependent charging effects were observed in the ETEM (in the form of apparent movement of the SiO film in the absence of gas), suggesting differences in the conductivity and therefore the temperature of the region of interest. Such effects can alter the results of kinetic modelling, which should therefore be regarded as semi-quantitative.

The model derived in Ref. [39], which describes a process that is first controlled by non-linear transport up to a thickness of 10 nm and then predominantly by linear diffusion up to full oxidation, provides consistent values for the NiO fraction from EELS for heating rates of 2 and 4 K min\(^{-1}\) (Fig. 8b). Measurements obtained for a rate of 6 K min\(^{-1}\) are shifted to lower temperatures by \(\sim40\) K. The activation energy \(E_a\) of 80/73 kJ mol\(^{-1}\) inferred for the reaction for 100/400 nm particles with \(R^2\) of 0.92/0.90 (Table 1) is similar, although slightly lower, to values usually reported in the literature (\(\sim100–200\) kJ mol\(^{-1}\) [1]).

It therefore appears that the reaction is limited by the diffusion of active species across the film rather than by the Ni/NiO and NiO/O\(_2\) interfacial reactions, in agreement with other similar oxidation processes [3].

4.3.2. Transition between non-linear and linear regimes

Non-linear effects accelerate the reaction during its initial stages. Their magnitude depends on the particle size
compared to the critical oxide thickness \( L_{\text{cr}} \) for the transition between non-linear and linear behaviour (10 nm here as in Ref. [40]). The use of values for \( L_{\text{cr}} \) above 10 nm, i.e., increasing the magnitude of non-linear effects, overestimates the fraction that is converted during the initial stages of the reaction. The value of 10 nm that was chosen appears to be an upper limit. For a particle size of 400 nm, built-in field effects are negligible when compared with uncertainties in the measurement and the entire reaction can be regarded as an apparently linear process (similar to that derived in Ref. [38]). For a particle size of 100 nm, the reaction rate is enhanced at lower conversion fractions (\( x < 0.2 \)), resulting in a slightly higher coefficient of determination (0.92 compared to 0.90; see Table 1). This result does not indicate that the latter description is better, as the difference arises from the fact that the modelled curve is closer to the first few points obtained at 6 K min\(^{-1}\), which are affected by a systematic error in the measurement (Fig. 8b). While non-linear diffusion of Ni\(^{2+}\) controls the growth of the first 3–4 nm of oxide formed in high vacuum conditions (not modelled in the kinetic fitting procedure) and perhaps also influence the formation of oxide up to a thickness of <15 nm (the value of \( L_{\text{cr}} \) added to the initial 3–4 nm), it appears that most of the process can be seen as apparently linear and thermally activated.

### 4.3.3. Diffusion mechanism

The rate constants that are obtained from EELS are consistent with values measured when oxidizing 5 µm Ni particles in 1.01 bar of O\(_2\) in a thermogravimetry apparatus [50], providing confidence in the reliability of the results acquired in situ in the ETEM (Fig. 9). The rate constants obtained here are also close to those predicted when linear diffusion of Ni\(^{2+}\) along the NiO grain boundaries controls the reaction [6]. Alternatively, the values predicted solely on the basis of Ni\(^{2+}\) lattice diffusion are several orders of magnitude lower [6,43]. Figs. 3 and 4 suggest that mass transport of Ni\(^{2+}\) is faster than that of O\(^{2-}\). Based on this kinetic analysis, it can be deduced further that diffusion of Ni\(^{2+}\) along NiO grain boundaries is likely to play a significant role in the oxidation process observed in the ETEM.

This picture is, however, still oversimplified. The activation energy for oxidation measured here (~70–80 kJ mol\(^{-1}\); Table 1) is lower than that expected for a process that is controlled solely by linear diffusion of Ni\(^{2+}\) along NiO grain boundaries (171 kJ mol\(^{-1}\) [3]). Different mechanisms that each contribute to the decrease in \( E_a \) must be included in the description. First, the density of grain boundaries evolves during the part of the reaction that is modelled as the NiO crystallite size changes from 3–4 nm to ~30 nm (Fig. 5b). The reaction rate is enhanced at the beginning of the reaction when compared to that at its end and in turn \( E_a \) is lowered [3]. In addition, a space charge separation region should occur close to the interfaces [3]. This region is estimated to have a thickness of ~10–100 nm, which is significant when compared to the particle size of 100–400 nm. Local electrical neutrality in the oxide film is therefore unlikely to be a fully valid assumption, especially in the presence of the electron beam. As a consequence, the transport of ions, such as the diffusion of Ni\(^{2+}\) along NiO grain boundaries, is likely to be field-assisted to an extent. This effect is probably more significant during the initial stages of oxidation (when the oxide is thin and further away from local electrical neutrality), which could decrease the value of \( E_a \) for the process. Other effects that are observed but not taken into account in the kinetic model include permeation of O\(_2\) through NiO cracks and thus direct formation of NiO and nucleation of voids at the Ni/NiO interfaces, which disrupts the supply of Ni\(^{2+}\) to the oxide film in some regions (both effects are seen in Fig. 4). The latter effect results in Ni self-diffusion, along with that of Ni vacancies, to maintain contact between the Ni particle and the NiO film. The overall Ni/ NiO contact area should decrease with increasing \( x \) and in turn lower \( E_a \).

### 4.4. Factors affecting ETEM observations

The high-energy electron beam may affect ETEM observations, as described in detail by Egerton et al. [51]. Buckett and Marks investigated the effect of electron irradiation on NiO [52]. An assessment of electron beam effects during NiO reduction in an environmental TEM can also be found in our previous study [27].

In order to understand the influence of the electron beam on the measurements, areas of interest were compared every 100 K with regions that had not been illuminated previously. No significant structural differences were observed between irradiated and non-irradiated areas between room temperature and 600 ºC.

However, electron beam effects may introduce more subtle artefacts. As discussed above, the movement of charged species that drive the oxidation process can be influenced by the electron beam. These effects are difficult to investigate. However, the rate constant for the reaction measured here is consistent with values obtained using thermogravimetry, providing confidence that such effects do not alter the growth-controlling mechanism significantly.

The electron beam may also increase the local specimen temperature and accelerate the reaction. This effect was not considered to be problematic here. The electron dose was kept constant in all three kinetic experiments, which should result in similar local increases in temperature. As the thermocouple is welded onto the outside of the furnace, the region of interest is likely to be at a slightly lower temperature when compared to the measured value. This difference is difficult to estimate. However, a systematic error does not influence the value of the measured activation energy significantly. Indeed, \( E_a \) only decreases by ~10 kJ mol\(^{-1}\) if the temperature of each measurement point is decreased artificially by 30 K. As only a semi-quantitative description of the process is sought, the latter two effects are not considered to be significant.
4.5. Qualitative description of the oxidation mechanism of Ni particles

The oxidation mechanism of the metallic Ni particles observed here is summarized schematically in Fig. 10. Growth of the first 3–4 nm of oxide (Fig. 10b), which occurs at room temperature in 10⁻⁷ mbar of O₂, is not thermally activated and appears to be controlled by built-in field effects, as described by Cabrera and Mott [4]. This NiO film does not grow significantly upon increasing the temperature to 250 °C, when an apparent linear diffusion process starts (Fig. 10c). Ni²⁺ is then observed to diffuse faster than O₂, resulting in the formation of voids at the Ni/NiO interfaces. The modelling procedure suggests that linear diffusion of Ni²⁺ along NiO grain boundaries is an important rate-controlling mechanism. However, this description is incomplete. First, the oxide film is not in a steady state on these length scales, which affects the diffusion of Ni²⁺ across the NiO. This effect is likely to be increased by the presence of the electron beam. Second, interface recession and the movement of dislocations do not balance the nucleation of voids at the Ni/NiO interface. Contact between the Ni and NiO may therefore be lost in some regions, hindering the reaction locally. Ni must then self-diffuse, along with vacancies, to continue the oxidation process in some regions. Curved edges of the particles may rupture locally due to geometrically induced stresses, allowing direct reaction between O₂ and freshly exposed Ni. As a result of all these effects, both polycrystalline NiO grains with irregular geometries and voids are observed (Fig. 10d).

5. Conclusions

Several different TEM and STEM imaging techniques, SAED and core-loss EELS have been applied in combination in an environmental transmission electron microscope, in order to investigate the structural and chemical changes that occur at the nanoscale during the oxidation of Ni particles in 3.2 mbar of O₂ at temperatures of up to 600 °C. By making use of changes in the shapes of the Ni L₂,₃ ionization edges, the reaction kinetics could be inferred and compared with models to assess the mechanism that controls the reaction and its relationship to the observed structural changes.

Although our approach is only semi-quantitative as a result of several limitations (including electron beam effects and the precision of the EELS and temperature measurements), the observed chemical changes could be correlated directly to changes in microstructure. Such comparisons are not possible using more conventional kinetic analysis techniques (such as thermogravimetry, X-ray diffraction and differential scanning calorimetry). Models describing the reaction kinetics were compared to the observed microstructure and local transient processes were resolved in situ.

Nucleation and growth of the first few nm of NiO on Ni was observed to occur rapidly at room temperature in high vacuum conditions as a result of built-in field effects. When O₂ was introduced at a pressure of 3.2 mbar and the temperature was increased in increments up to 600 °C, inhomogeneous randomly oriented NiO crystallites and voids formed as a result of several different mechanisms: Ni²⁺ diffusion along NiO grain boundaries (probably field-assisted), self-diffusion of Ni²⁺ and Ni vacancies and the formation of transverse cracks in the NiO film, creating channels for O₂ permeation towards unreacted Ni. The formation of transverse channels in NiO had been predicted to occur on the basis of post mortem observations and acoustic emission studies but to the knowledge of the authors had not previously been visualized in situ at this spatial resolution.

The oxidation mechanisms are likely to be affected to an extent by the presence of the electron beam. However, the NiO structures that were obtained in situ in the present study are comparable to those reported on the basis of ex situ studies in the literature. The overall reaction rate also corresponds to that measured using other methods, providing confidence that the mechanisms observed in situ in the environmental transmission electron microscope are representative.

While the present methodology provides new insight into the oxidation mechanism of Ni particles, additional work is required to obtain a fully quantitative description of the process. One of the most important unknown...
parameters is the strength of the electric field in the NiO film during oxidation.

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Appendix A. Supplementary material

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References