

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

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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 O₂ 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 Ni²⁺ along NiO grain boundaries, self-diffusion of Ni²⁺ 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 [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 [3]. The first model is denoted the Mott–Cabrerá theory and describes non-linear growth of a thin oxide film [4] (below ~10 nm for NiO [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 [5] (above ~1 μm for NiO at 500 °C [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 Ni²⁺ through the NiO lattice controlling the growth rate. At lower temperatures, Ni²⁺ diffusion through the oxide grain boundaries must be included in the description [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 [7].

The microstructure that forms during Ni oxidation is closely related to the growth-controlling mechanism.

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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 μm 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 Ni(O), 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™ (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 ~ 50 nm using optical diffraction, with an average agglomerate size of ~ 990 nm, while the average crystallite size was measured to be ~ 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 $2 \text{ ml}_N \text{ min}^{-1}$ 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

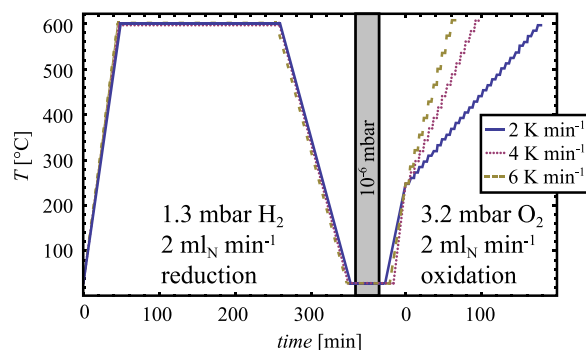


Fig. 1. Time and temperature parameters used to reduce the NiO particles isothermally and then to re-oxidize the resulting Ni particles to NiO, while ramping the temperature at equivalent average rates of 2, 4 or 6 K min^{-1} . A separate set of measurements (involving the acquisition of an image, a diffraction pattern and an EEL spectrum) was performed at each step in each ramp.

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