Nickel Oxide Reduction by Hydrogen: Kinetics and Structural Transformations

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ABSTRACT: We studied the reduction kinetics of bulk NiO crystals by hydrogen and the corresponding structural transformations in the temperature range of 543−1593 K. A new experimental approach allows us to arrest and quench the reaction at different stages with millisecond time resolution. Two distinctive temperature intervals are found where the reaction kinetics and product microstructures are different. At relatively low temperatures, 543−773 K, the kinetic curves have a sigmoidal shape with long induction times (up to 2000 s) and result in incomplete conversion. Low-temperature reduction forms a complex polycrystalline Ni/NiO porous structure with characteristic pore size on the order of 100 nm. No induction period was observed for the high-temperature conditions (1173−1593 K), and full reduction of NiO to Ni is achieved within seconds. An extremely fine porous metal structure, with pore size under 10 nm, forms during high-temperature reduction by a novel crystal growth mechanism. This consists of the epitaxial-like transformation of micrometer-sized NiO single crystals into single-crystalline Ni without any crystallographic changes, including shape, size, or crystal orientation. The Avrami nucleation model accurately describes the reaction kinetics in both temperature regimes. However, the structural transformations during reduction in both nanolevel and atomic level are very complex, and the mechanism relies on both nucleation and the critical diffusion length for outward diffusion of water molecules.

INTRODUCTION

Nickel is an important industrial catalyst and is typically produced by reduction of nickel oxide (NiO).1−5 This metal is also a promising oxygen carrier in chemical looping combustion, which is a novel approach for green power generation.6−8 NiO reduction and the subsequent Ni behavior in hydrogen are of practical importance in solid oxide fuel cells9,10 where it determines the structure of the electronic conductor on the anode side. It is also a model process for the investigation of oxide reduction mechanisms11−15 due to its single-stage transformation, as compared to Fe2O316−19 and CuO20−23.

Despite extensive investigations of NiO reduction by hydrogen since the pioneering work23 of Benton and Emmett in 1924, many questions remain about its kinetics and the related structural transformation mechanism. For example, the reported activation energy varies by an order of magnitude, between 10 and 150 kJ/mol2,11,14−26. This large variation may be explained by the lack of consistency between NiO samples, characterization techniques, and other experimental parameters. Furthermore, different kinetic models, including reaction order,2 Avrami27−29 geometrical construction,26 and Szekely−Evans30,31 were proposed to describe this reaction.

Several in situ techniques were used to investigate the mechanism of NiO reduction. Richardson et al. studied2 the reduction of porous NiO particles by hydrogen using a time-resolved X-ray diffraction technique in the temperature range of 450−570 K. A three-step reaction mechanism was proposed: (i) nickel clusters form during an induction period; (ii) next, the reaction rate accelerates as the clusters grow; (iii) finally, the process settles to a pseudo-first-order reaction with respect to nickel. Jangros et al. (573−923 K) used environmental transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy for in situ study of hydrogen reduction of NiO.11 On the basis of a model-based fitting procedure, they suggested that the Avrami (nucleation and nuclei growth) model describes the reaction. This assumes that hydrogen molecules predominantly dissociate on nickel atoms.
that are surrounded by oxygen vacancies. Rodriguez et al. used synchrotron time-resolved X-ray adsorption and diffraction techniques to study the reduction of single-crystalline and polycrystalline NiO between 523 and 620 K. They found a strong correlation between the rate of reduction and the amount of oxygen defects in the metal oxide structure. It was suggested that the presence of oxygen vacancies increases the adsorption energy of H₂ on the oxide surface, as well as decreases the energy barrier for hydrogen dissociation. H atoms then diffuse to the NiO reaction sites, resulting in a rupturing of the Ni=O bond with simultaneous desorption of a water molecule.

Studies using optical microscopy by Utigard et al. led to the conclusion that the geometric construction, or shrinking core, model represents the reduction kinetics of NiO granules in the range of 100–500 μm. This model assumes that, after the reduction reaction has begun, the solid particles consist of a nonreacted core encased in a uniform layer of the reaction product. These two regions are sharply separated from each other by a well-defined interface. As the reaction proceeds, diffusion of hydrogen through the Ni layer becomes the rate-limiting step. Later, Plascencia and Utigard showed that the reduction of large porous NiO particles can be described by the grain model proposed by Szekely et al. In this empirical model, a particle is considered to be an agglomeration of individual grains, and each of them undergoes a microscopic shrinking core reduction. Depending on the process conditions and characteristics of NiO, either chemistry (low temperatures, high porosities) or internal diffusion (high temperatures, low porosities) controls the reaction kinetics.

Recently, Hidayat et al. identified several distinctive porous microstructures, during the reduction of bulk dense NiO samples. Jeangros et al. also reported the macropore (50–100 nm) formation during early stages of NiO nanoparticle reduction by hydrogen. However, toward the end of reduction, the pores disappeared. The severe collapse of pores has also been reported during the reduction of hollow NiO nanoparticles at 550–870 K. Evidently, hydrogen reduction of nickel oxide is a complex structural transformation. The mechanism of NiO reduction by hydrogen is suggested based on direct correlations between reaction kinetics and the observed structural transformations at the micro- and nanolevels and atomic levels.

### EXPERIMENTAL SECTION

The experiments were performed using partially oxidized nickel wires (Supporting Figure S1). To prepare these specimens an initial Ni wire (purity = 99.995%, 100 μm, and 8.5 cm in length) was heated by direct current to 1573 K and retained at this temperature for 150 s in air. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 1A,B) illustrate that the formed NiO layer is polycrystalline with grain size in the range of 1–3 μm. Analysis of the selected area electron diffraction pattern (Figure 1C) and high-resolution TEM images (Figure 1D) reveal that the NiO/Ni wires are pore-free single crystals.

A reaction chamber equipped with infrared-transparent windows, high-speed solar cell-based temperature sensors, a power source, and a PC-controlled unit (Supporting Figure 2) was used in this hydrogen reduction experiment (Supporting Figure 2). The reaction setup allows rapid (up to 4.5 x 10⁵ K/s) controllable heating of the wires (Supporting Figure 3) and continuous data (temperature, electrical power, resistivity of the wire) acquisition with a frequency of 10 kHz (see details in the Supporting Information). These NiO/Ni wires were inserted into the chamber, which was then evacuated to 10⁻³ kPa, purged with pure hydrogen, and finally filled with H₂ to the desired pressure from 1.0 to 7.0 kPa. Following each experiment, no pressure change was observed. Utilizing the internal Ni metallic core, the wires were controllably heated by direct current to the desired temperature (543–1593 K). The termination of electrical current through the thin wire allows rapid arresting of the process with a quenching rate of ~10⁶ K/s (Supporting Figure 3). This feature permits both arresting of the reaction and preservation of the sample structure with millisecond time resolution.

A Mettler-Toledo balance (measuring accuracy of 10⁻⁵ g) was used to obtain the sample weight at different stages of the process to determine the degree of conversion (α) during reduction reaction as

\[ α = -\Delta m / \Delta m_0 \]

where \( \Delta m_0 \) is the mass change of Ni wire after initial oxidation and \( \Delta m \) is the subsequent mass change of the Ni/NiO wire during the reduction reaction.

Obtained kinetic curves were analyzed using custom Matlab nonlinear least-squares regression analysis. A variety of models, totaling 18, were tested, including reaction order, geometrical...
contraction (R1, R2, R3), one-, two-, or three-dimension diffusion-limited (D1, D2, D3), Avrami–Erofeev (AE) nucleation models, and others. The fitting parameters including pre-exponential factor ($k_0$), activation energy ($E_a$), and exponential term ($n$) were varied for each model, with the two-parameter models having only $k_0$ and $E_a$ fit. All models were analyzed in series, with the varying parameters ranging over 20 log units of perturbation over the local attempt-space. The results with the highest goodness of fit ($R^2$) were compared across models. Each kinetic data set was analyzed both individually and in every inclusive range. The inclusive data sets with the best goodness of fits were interpreted to be within the same kinetic regime.

SEM and TEM were employed to characterize the composition and morphology of the reaction products, as well as the atomic structure of the materials. SEM analysis was conducted on a Magellan 400 (FEI, USA) with a resolution of 0.6 nm. The Magellan 400 is equipped with an energy dispersive X-ray spectrometer (EDS, Bruker) with energy resolution of 123 eV. A Titan 80-300 (FEI, USA) transmission electron microscope, with resolution of 0.136 nm in scanning TEM mode and about 0.1 nm information limit in high-resolution TEM mode, was used. The Titan is equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford Inca) system with spectral energy resolution of 130 eV.

A Helios NanoLab 600 system (FEI) with dual electron/ion beam was used to produce cross sections of reacted wires by ion milling with a gallium ion beam. First, a ∼2 μm thick layer of platinum in a 15 μm × 1 μm rectangular area was deposited onto the selected sample. Next, a trench with ∼10 μm width, ∼15 μm length, ∼7.5 μm depth, and a 45° base angle was milled on the particle surface under an accelerating voltage of 10 kV with a milling current of 27 nA. Then, a 40 nm thick layer was milled into the side wall of the trench under an accelerating voltage of 10 kV and a milling current of 700 pA to produce a clean cross section without milling artifacts. Thereafter, the electron beam was used to image the side wall of the trench at an angle of 52° parallel to the side wall. The TEM samples were also prepared using a Helios NanoLab 600 system by making cross-sectional slices from the top surfaces of the wires. The slice and view (S&V, FEI) software package was used on the Helios NanoLab 600 to collect a series of sequential images. A voltage of 30 kV with a milling current of 9.7 pA was used to make a series of 100 images with ∼10 μm width and ∼7.5 μm depth. These images were taken in series after milling 10 nm between each image, leading to a particle volume of ∼75 μm$^3$ imaged throughout and prepared for pore characterization.

**RESULTS**

Below we report the kinetics for NiO reduction by hydrogen at different temperatures (e.g., 543, 608, 1503, and 1593 K) at constant H$_2$ pressure (e.g., 1.33 and 6.67 kPa), as well as the characteristic structures of the reaction media on micro- and nanoscales and atomic scales at different stages of the process.

**Reaction Kinetics.** Kinetics curves of NiO reduction by hydrogen, which represent the degree of conversion ($\alpha$) versus time ($t$) at different temperatures and constant H$_2$ pressure, are presented in Figure 2. It can be seen that, at 543 K (Figure 2A) and 608 K (Figure 2B) and 608 K (Figure 2B), the kinetic curves have a sigmoidal shape with low reaction rates at initial stages, followed by a significant acceleration of the process after some critical time (induction period). Supporting Table 1 shows that the induction period depends on the temperature and pressure and can be as long as 2000 s. Another important observation is that full conversion cannot be achieved.

The kinetics curves at 1503 K (Figure 2C) and 1593 K (Figure 2D) possess different behaviors. No induction period is detected and the degree of conversion monotonically increases with time in a nonlinear (parabolic) fashion. Figure 1D also
The results of model-based fitting analysis for 608 and 1503 K temperatures are shown in panels B and C of Figure 2, respectively. Kinetic data at 608 K fits with $R^2 = 0.98$ by using the AE$_n$ model with a value of exponent $n = 0.58$ (Figure 2B). The kinetic data for 1503 K can be also accurately ($R^2 = 0.99$) fit by the AE$_n$ model with $n = 0.95$ (Figure 2C), as well as by the D1 model ($R^2 = 0.95$). All other models show less fitting accuracy.

Figure 3 shows the $n$ parameter as a function of temperature over the entire studied range. In low temperatures (543–773 K), the parameter $n$ does not vary. This would imply that both nucleation and a diffusion-related process slow the reaction rate. At high temperatures (1173–1593 K), the AE$_n$ model fits each individual kinetic curve. However, in this case, the Avrami exponent increases with temperature, approaching 1. As the temperature increases, nucleation becomes less important, but the diffusion limitation remains.

The activation energies of nickel oxide reduction determined by model-based fitting analysis are $\sim 84$ and $\sim 109$ kJ/mol for the low- and high-temperature ranges, respectively. These values are comparable to previously reported data in the literature.\textsuperscript{11,26} To validate the kinetic modeling, the structural transformations were studied.

**Microstructure Transformation.** We selected samples heated at 608 and 1503 K (under 6.67 kPa) with different reduction times to investigate the relationship between structural transformations and the reduction kinetics. Figure 4 summarizes the microstructure analysis of the samples reduced at early stages of the reaction for both temperatures. A porous structure is predominantly formed on the crystal vertices close to the boundaries between the NiO grains after the sample had been heated at 608 K for 50 s (Figure 4A). However, this structure accounts for $<1\%$ the total wire surface. EDS analysis of the cross sections (Figure 4B) shows approximately 35 at. $\%$ O and 65 at. $\%$ Ni in these porous regions. Kinetic data in Figure 2B suggest that the degree of conversion for this sample is essentially zero, indicating that Ni nucleation occurs on the edges of the NiO grains forming porous Ni-rich areas.

Figure 4C illustrates the wire surface after heating to 1503 K for only 0.007 s. The facets that are present on the initial NiO grains are not apparent after this short reduction time. The surface, however, involves two characteristic regions with different contrasts. EDS analysis reveals that the darker areas contain oxygen and nickel, whereas the lighter ones are pure Ni. The cross section (Figure 4D) of this surface shows a relatively uniform, $\sim 300$ nm thick, layer, which consists of a primarily pure Ni phase with some NiO residue. This indicates that, at 1503 K, nucleation is essentially instantaneous, and the following growth of the reduced layer is very fast (at a rate of $\sim 40 \mu m/s$).

SEM analysis of the samples with significant degrees of conversion is shown in Figure 5. Figure 5A shows that the grain size on the surface of a wire, after reduction at 608 K for 300 s, is similar to that of the initial NiO (see Figure 1A). Reduction at 608 K leads to the formation of macropores, which range from 50 to 100 nm and are uniformly distributed along the grain surfaces. The cross section of this sample contains two distinct layers, one with a complex porous structure and the other pure NiO (Figure 5B). Utilizing sequential cross sections (Video 1S) it is observed that the pores form a continuous network of channels throughout the reduced layer, originating from grain boundaries or the outer wire surface (Supporting Information Figure 4; Video 1S).

A different structure is observed after reduction at 1503 K for 8 s (Figure 5C). The topology of the sample surface is much smoother and contains no macropores compared to the low-temperature reduction. A cross section of the sample shows that a uniform, oxygen-free Ni layer forms on the surface of the
wire, with a sharp interface separating this and the NiO layer (Figure 5D).

High-resolution EDS profiles of the sample, heated at 608 K for 300 s, measured across the reacted layer show approximately 25 at. % O and 75 at. % Ni (Figure 6A), indicating ∼0.5 degree of conversion. This analysis is in good agreement with the degree of conversion measured by the sample weight change (Figure 2B). EDS profiles also show that, closer to the nonreduced NiO grains, the concentration of Ni gradually decreases to 50 at. % with a simultaneous increase of O to 50 at. %. The profiles of the reduced layer heated at 1503 K for 8 s (Figure 6B) indicate that the Ni concentration is ∼100 at. %. An abrupt decrease of nickel and a simultaneous increase of O to ∼50 at. % take place at the interface between the reduced and nonreduced layers.

TEM analysis for both samples heated at 608 and 1503 K are shown in Figures 7 and 8, respectively. A bright field TEM image (Figure 7A) of the sample reduced at 608 K shows a transitional area between the reduced layer and the original NiO grain. The electron diffraction pattern (Figure 7B) of the reduced layer contains two distinct phases; fine polycrystalline Ni (scattered rings) and single-crystalline NiO (big bright spots). Bright field TEM (Figure 7C) of the reduced layer shows that pore-free NiO grains are transformed into a complex NiO–Ni porous structure, with both phases in well-defined regions. The fine polycrystalline Ni occurs along the pore walls within a single-crystal NiO skeleton. High-angle annular dark field scanning TEM (Figure 7D) together with EDS analysis suggests that the brighter phase, closer to the surface of pores, is Ni, whereas the darker one is NiO.

TEM studies reveal that, at high temperatures, NiO grains convert into Ni without changing the grain geometry, including shape, size, or crystal orientation (Figure 8A,B). The reaction forms a network of mesoporous channels, ranging from 5 to 15 nm, that end at the grain boundaries (Figure 8C) or at the wire surface. Figure 8D shows the nanosized pores at the Ni/NiO interface and the corresponding channels.

### DISCUSSION

The kinetics of nickel oxide reduction by hydrogen were extensively studied using both supported and unsupported (bulk) samples. In this work we use unsupported polycrystalline samples with 1−3 μm single-crystalline NiO (Figure 1A,B). Different kinetic models were suggested to describe the hydrogen reduction of NiO with similar characteristics. Formal
Ni interface (D). single crystalline Ni layer (C), and high-resolution TEM image NiO/ coats the inner structure of the channels.

Channel growth proceeds both into the bulk and by generation of water vapor that di pone-free NiO remains constant. The reduction is accompanied will be converted into a porous structure upon complete di tting, forming the polycrystalline Ni nanolayer that radially outward, forming the polycrystalline Ni nanolayer that channels. This process is slow and takes hundreds to thousands of seconds to reach a measurable degree of conversion. Initial nucleation occurs. A sharp interface is evident between the unreacted NiO and completely reduced Ni. This may indicate that the geometrical construction or diffusion-limited (D1) models are suitable to describe the kinetics. However, the Avrami model best fits the kinetic data, suggesting instantaneous nucleation and one-dimensional growth. This implies that the Ni nucleation density on the outer surface of the NiO crystals is much higher than for low-temperature reduction. The increased nucleation density may be due to the higher equilibrium concentration of oxygen vacancies, which act as nucleation sites. As a result, a continuous layer of porous reduced Ni covers the entire wire surface and rapidly moves toward the core (Figures 3D and 9).

The number of channels is much higher than the low-temperature case, and the distance between them is <10 nm, which explains the absence of an induction period. Because of the remarkably high reduction rates (Figure 2C,D) and small distances (<2δ) between the channels, the NiO grains proceed to full conversion (Figure 9). Similar to the low-temperature reduction case, the channels are formed due to the shrinking of the cubic NiO lattice into cubic Ni. There are many similarities in the reduction process for both temperature ranges, whereas the main difference is the nucleation density. Due to this, the AE model better describes both kinetics. Owing to high nuclei density, the process proceeds only in the forward direction, without formation of polycrystalline Ni, so that the NiO grains epitaxialy transform into Ni without losing single crystallinity or changing the orientation.

Several studies reported the formation of both epitaxial and nonepitaxial Ni domains (islands) at the early stages of NiO reduction. However, the number of epitaxial Ni nuclei decreases as the reaction proceeds. It was shown that the loss of epitaxy results from the rotation of the Ni domains as they grow due to the appearance of cracks around them. It was also shown that the nonepitaxial Ni regions take longer to nucleate than the epitaxial ones, but grow faster when formed. These effects always induce randomly oriented polycrystalline Ni structures, similar to our samples reduced below 773 K.

At high temperatures (e.g., 1503 K) the initial epitaxial Ni nuclei do not have enough time to rotate due to instantaneous nucleation. The high initial nucleation density forms a thin epitaxial-like Ni layer on the outer surface of the NiO single

We have estimated that approximately 41% of the NiO volume will be converted into a porous structure upon complete reduction assuming that the overall crystal volume of the initial pore-free NiO remains constant. The reduction is accompanied by generation of water vapor that diffuses out through the channels. Channel growth proceeds both into the bulk and radially outward, forming the polycrystalline Ni nanolayer that coats the inner structure of the channels.
crystals; this leads to an increased NiO reduction rate in the lateral direction without any crystallographic changes.

**CONCLUSIONS**

Hydrogen reduction of 1–3 μm single-crystalline NiO grains was studied from 543 to 1593 K by scheduled rapid heating and quenching of Ni/NiO wires, coupled with ex situ electron microscopy of the reacted samples. Both kinetic data and structural observations are consistent with the Avrami nucleation model. Depending on the reaction temperature, two distinctive porous product structures were identified. At 543–773 K, noncomplete reduction results in a NiO−Ni product with a complex porous network structure due to the low nucleation rates and slow outward diffusion of water molecules. Above 1173 K, the increased nuclei density causes instantaneous nucleation of Ni on the whole NiO crystal surface, followed by rapid growth of Ni phase. A new crystal growth mechanism was observed for metal during the reduction of an oxide, where the atomic lattice of single-crystalline NiO transforms into Ni without any change in crystallography. In the 773–1173 K range, the product represents a mixed microstructure of both low and high temperatures. The kinetics of the process shows some distinctive features. These investigations currently are in progress and will be reported in a follow-up paper.

**ASSOCIATED CONTENT**

- Supporting Information
  Detailed temperature measurements and calibrations, heating and cooling temperature profiles, additional SEM images of Ni and NiO/Ni wires, and duration of induction periods; schematic representation of experimental setup. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04313.

- Web-Enhanced Features
  Web-enhanced video of “Slice and View” sequential SEM analysis is available as a video file in the HTML version of the paper.

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Notes
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