

Size-Dependent Nanoscale Kirkendall Effect During the Oxidation of Nickel Nanoparticles

Justin G. Railsback, Aaron C. Johnston-Peck, Junwei Wang, and Joseph B. Tracy

Department of Materials Science and Engineering, North Carolina State University,

ARTICLE ASAP

DOI: 10.1021/nn901736y

20 nm

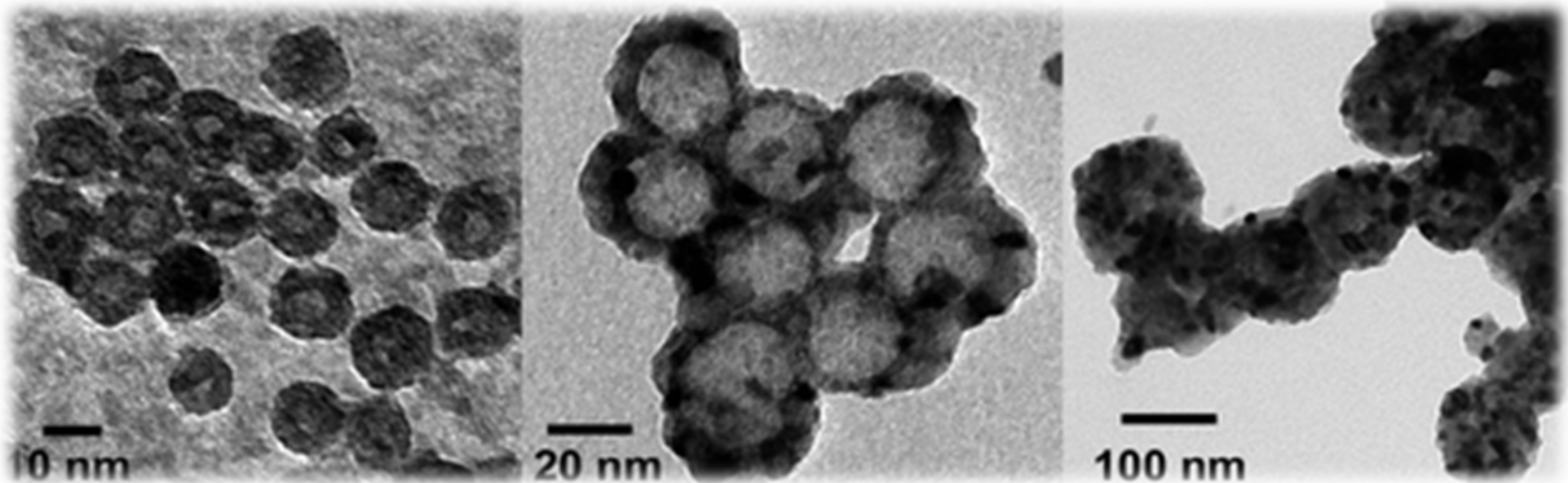
Sreeprasad T. S.
17-04-10

Introduction

- The Kirkendall effect- a vacancy flux and subsequent void formation resulting from diffusivity differences at inorganic interfaces.
- Nanoscale Kirkendall effect (NKE)- Solid metal NPs were converted to hollow metal oxide, sulfide, and selenide NPs.
- When outward diffusion of the metal cations is much faster than the inward diffusion of the anions, an inward flux of vacancies accompanies the outward metal cation flux to balance the diffusivity difference. When the vacancies supersaturate, they coalesce into a void (or in some cases, several small voids that usually merge into a larger void); the reaction products are hollow NPs with binary compositions
- Single void or multiple voids depending upon the speed of self diffusion

In this report

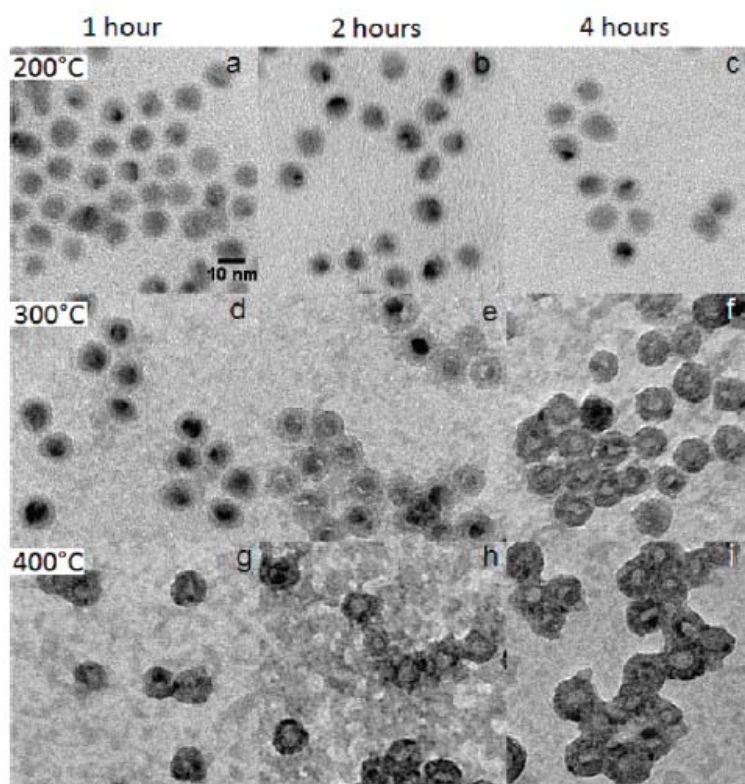
They report and discuss the mechanism of the *size-dependent NKE during the oxidation of Ni NPs in air* to form hollow (single void) or porous (multiple voids) partially or completely oxidized Ni/NiO NPs at different temperatures and times. There are marked differences in the symmetric, asymmetric, and porous nanostructures that are obtained from different sizes of Ni NPs.



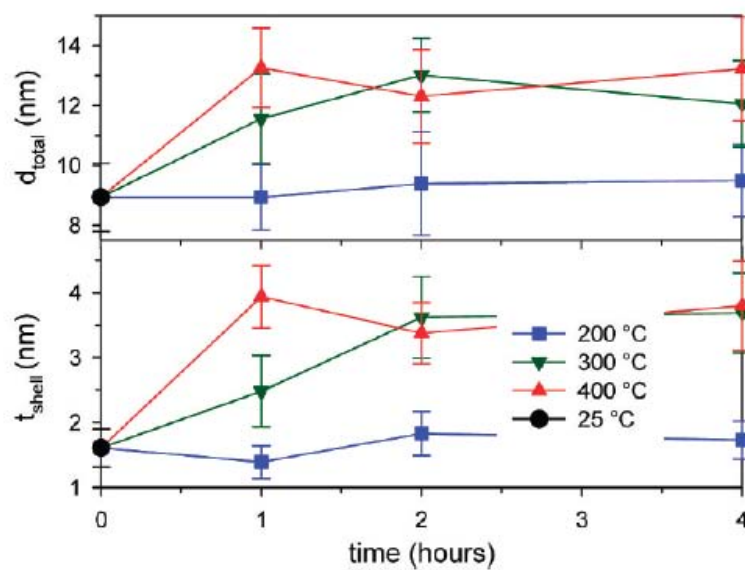
Methods

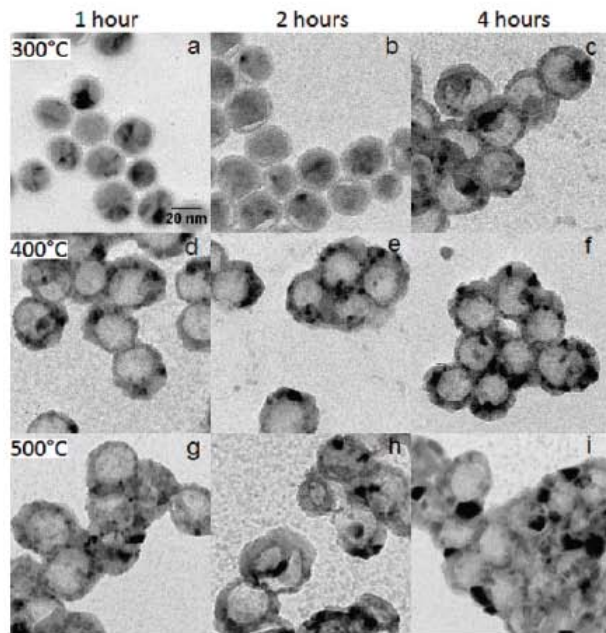
Nanoparticle synthesis : Ni(acac)₂, oleylamine, trioctylphosphine oxide (TOPO) or 1-octadecene (ODE) mixed and heated to 80°C under vacuum. Varying amounts of (TOP) were injected into the mixture before rapidly heating the solution to 240 °C (20 °C/min ramp rate) with vigorous stirring.

Oxidation Procedure : Ni NPs, a solution in hexanes was sonicated for one minute to improve their dispersion, and the mixture was drop cast onto SiO support films on Cu grids for TEM. The ligands were removed to facilitate oxidation by placing the grids in an ultraviolet light with ozone (UVO) cleaner for 4 min at room temperature. For each heat treatment time and temperature, a different TEM grid was used. Heat treatments were performed in air in a Protherm PC442 tube furnace at 200-500 °C for durations of 1-4 h.

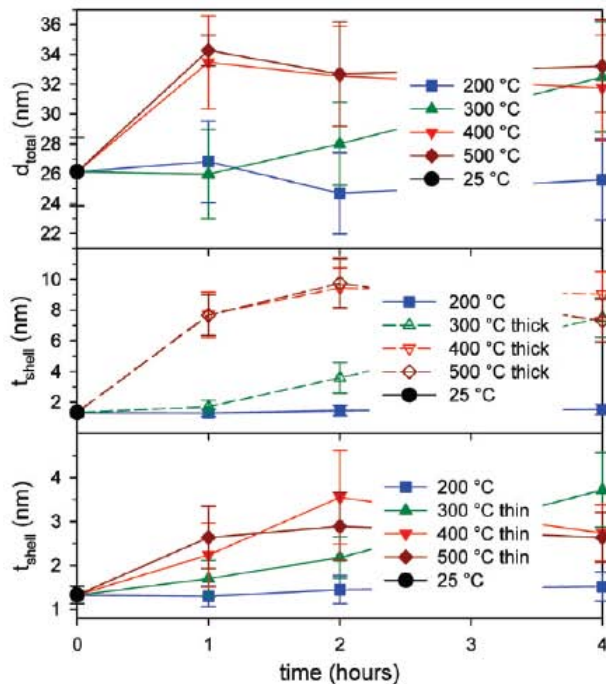
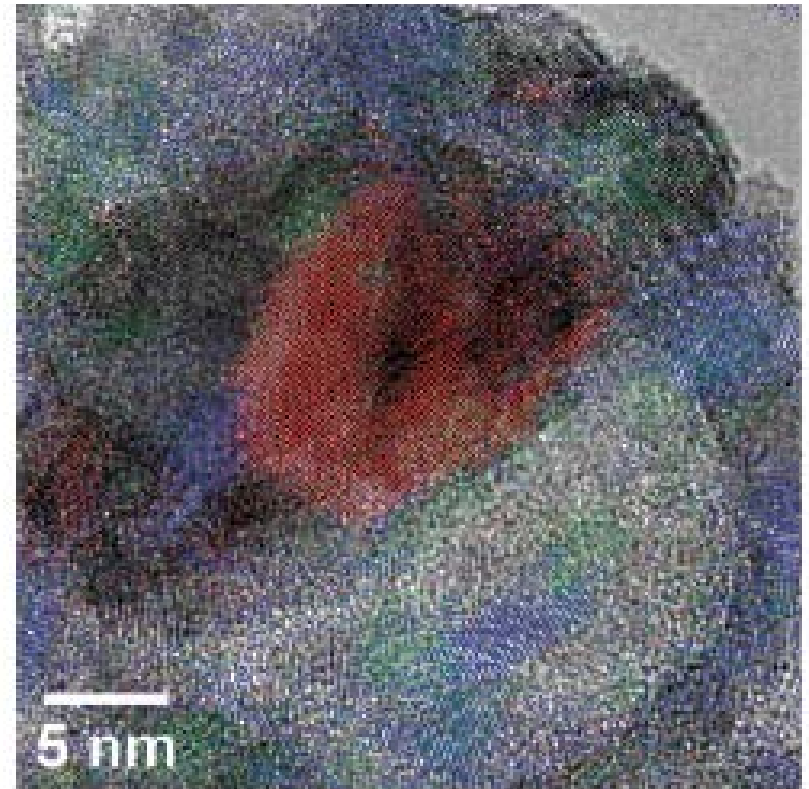


9 nm Ni NPs

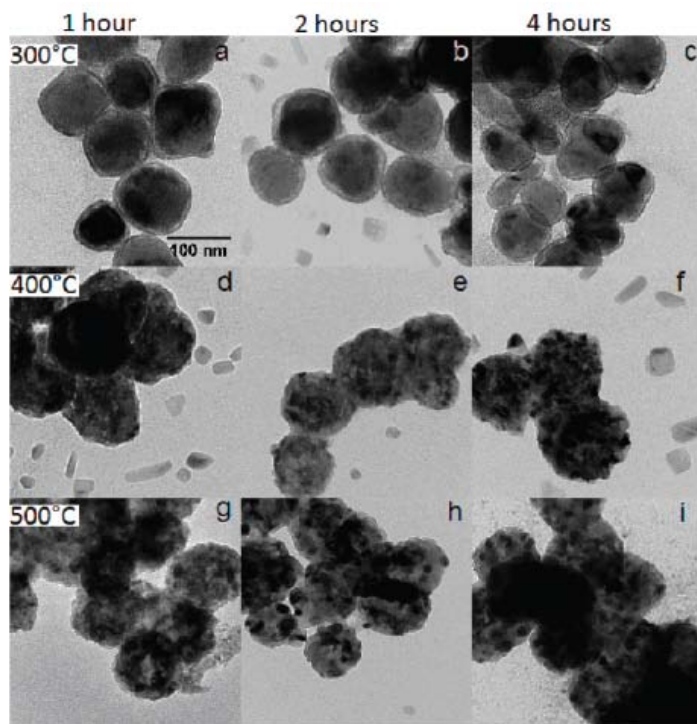




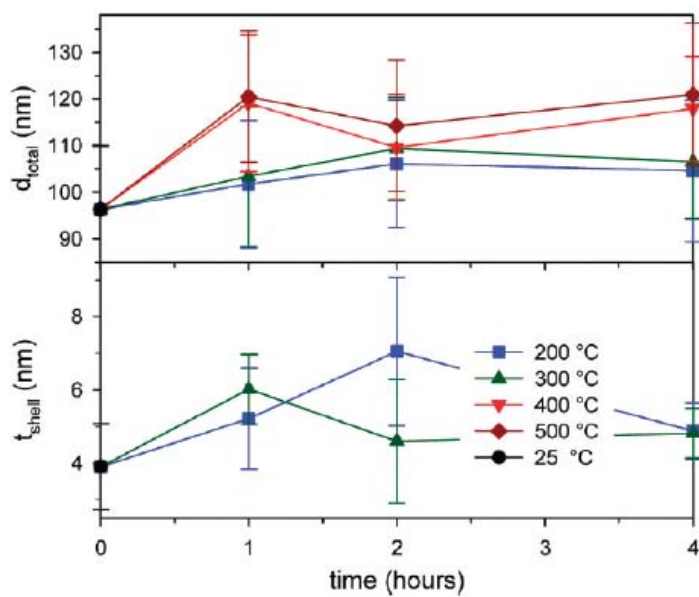
26 nm Ni NPs

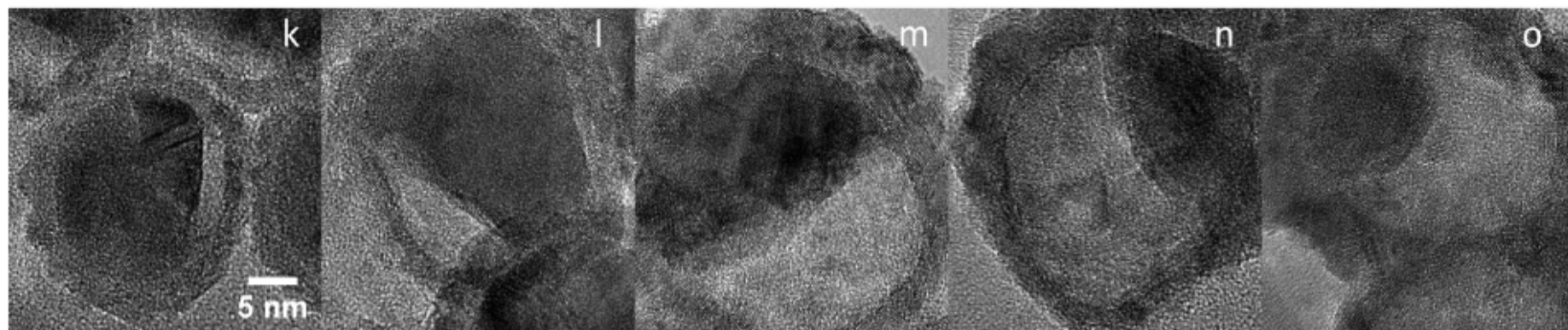
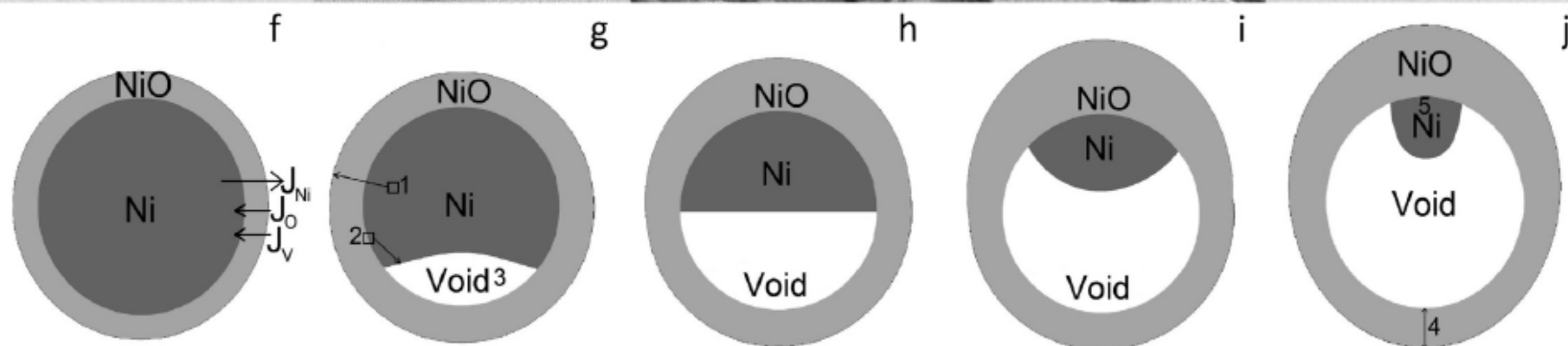
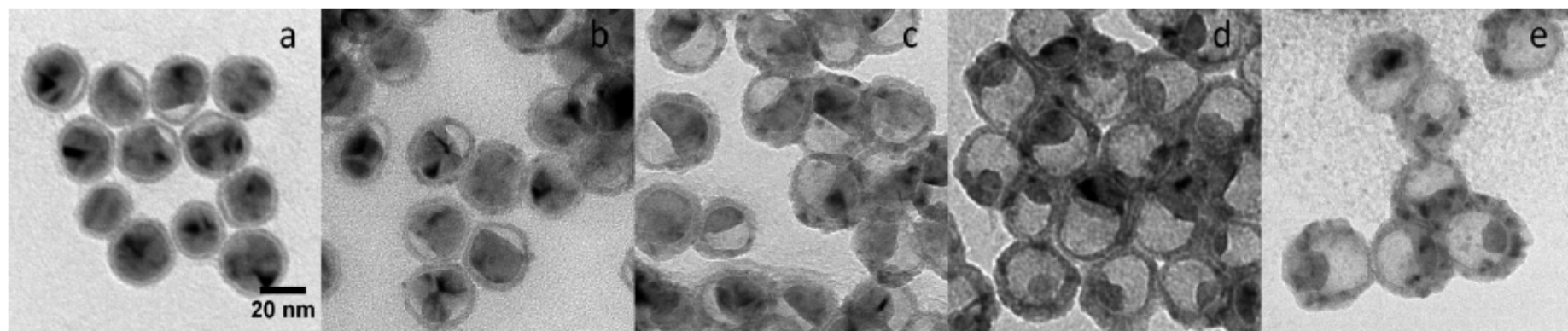


HRTEM image of a 26 nm nanoparticle after oxidation in air at 300 °C for 150 min. The overlaid colour layers represent lattice spacings for (red) Ni {200}, (blue) NiO {111}, and (green) NiO {220}. The Ni {111} and NiO {200}



96 nm Ni NPs





Conclusions

- ✓ Distinct size-dependent behaviours for the NKE in the Ni/NiO system were shown
- ✓ Fast self-diffusion of Ni compared with its rate of diffusion through the NiO shell results in single voids for the smaller sizes (9 and 26 nm), but multiple voids form in the 96 nm NPs, because self-diffusion is not fast enough to cause the voids to combine into a single void.
- ✓ NiO shell results in single voids for the smaller sizes (9 and 26 nm), but multiple voids form in the 96 nm NPs, because self-diffusion is not fast enough to cause the voids to combine into a single void.
- ✓ Oxidation occurs most quickly at elevated temperatures. but final structures do not depend on the oxidation temperature.