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TEM/STEM Analysis of NiO Reduction to Ni during Annealing in H_2 Atmosphere

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Nickel oxide (NiO) reduction to Ni during annealing in hydrogen gas (H2) atmosphere is of practical interest for catalytical applications [1] and for production of metallic Ni [2] particles. Recent in-situ TEM study [3] using monitoring of structure changes by EELS indicated that Ni reduction proceeds by Ni nucleation on NiO surface with further growth of Ni crystallites (often expitaxially) and the movement of growth front that is accompanied by the formation of pores within the NiO grains to accommodate the volume shrinkage associated with the reduction process. While this study was performed on NiO powder, the present study was focusing on structure evolution in bulk polycrystalline material.

The Ni wires were originally fully oxidized to NiO. The NiO wires were reduced to Ni during annealing at 1230^{o}C in hydrogen atmosphere (50 torr). The samples were analyzed in HRTEM and HAADF STEM modes using FEI Titan 80-300 electron microscope. The microscope was operated at 300 keV and equipped with an Oxford Inca EDX detector. A TEM cross-sectional sample that included the NiO-Ni interface was prepared from the top surface by Focus Ion Beam (FIB) using FEI Helios SEM/FIB dual beam equipment.

As one can see from the cross sectional TEM and STEM images of Figure 1, the material is polycrystalline with relatively large grains (several um in diameter) that contains also large voids probably due to the volume shrinkage associated with the reduction process. EDS (Fig. 2a) indicated that Ni grains have almost no oxygen. The Ni grains have porous structure with small channels elongated almost parallel to some crystallographic directions (Fig. 2b) that may indicate on anisotropic oxidation during reduction process. The diameters of channels are ranging from 15 to 20 nm, they form a net. The formation of the porous channels is associated with the volume shrinkage due to conversion of NiO to Ni. During this process the crystalline structure of Ni is following crystalline lattice of NiO thus resembling the epitaxy as it was concluded earlier [3]. The oxygen from NiO is reacting with hydrogen which results in formation of the water molecules. The water vapor that is formed during high temperature reduction process can easily be transferred to the surface thus to provide a fast kinetic pathway for the reduction.

References:

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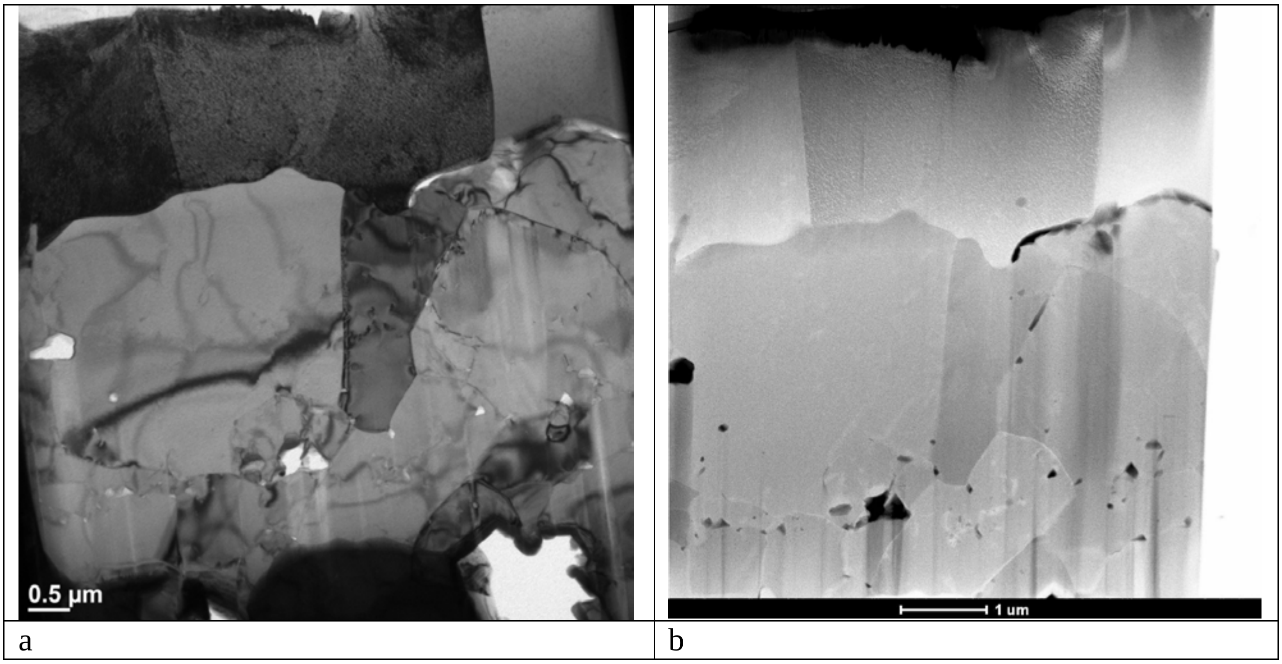

Figure 1. Cross-sectional TEM (a) and HDAAF STEM (b) images of Ni-NiO sample.

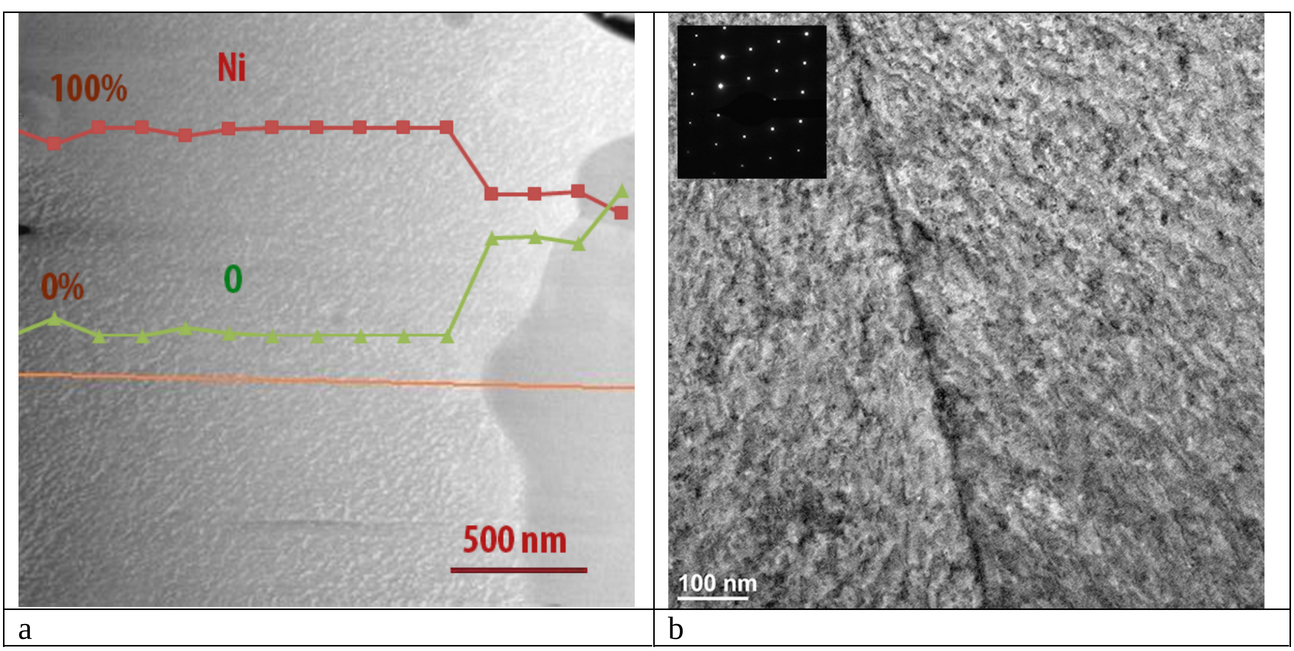

Figure 2. Cross-sectional HDAAF STEM (a) and TEM (b) images of Ni-NiO sample. Inserted are EDX profiles of Ni and O in the sample across the Ni-NiO interface (a) and electron diffraction pattern (b).

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