

BRIEF COMMUNICATIONS

Effect of Shear Deformation under High Pressure on NiO Structure Transformation in Reducing Atmosphere

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The process of NiO structure reconstruction under reduction treatment by a CO/H₂ mixture has been studied using *in situ* X-ray powder diffraction and transmission electron microscopy. It was found that there are two different forms of phase transformation (NiO → Ni₃C and NiO → Ni) depending on the microstructure of the initial NiO specimen. © 1992 Academic Press, Inc.

1. Introduction

Bulk nickel oxide (NiO) is a common catalyst precursor for methane formation from CO and H₂ (1-3). In the atmosphere of the reaction mixture, metallic nickel and/or nickel carbide forms. It is well known that lattice distortions plays a significant role in reduction and carbidization processes (4), but it has not been reported that defects could substantially affect the direction of oxide structure transformation.

We have studied the influence of the dislocation network created through shear deformation under high pressure on NiO structure changes in a CO/H₂ atmosphere. The microstructure of the initial NiO specimens was found to be the main influence on the

formation of different phases in a reducing atmosphere, i.e., metallic Ni or Ni₃C.

2. Experimental

An initial NiO(I) sample was prepared by calcination of nickel carbonate in air at 700°C for 3 hr. A "loaded" NiO(II) specimen was obtained from an NiO(I) sample by shear deformation under high pressure (SD + HP) on a Bridgeman anvil (20 kbar, 140°C, cycle regime).

X-ray powder diffraction (XRD) experiments have been carried out *in situ* at 240°C in a 1 : 1 CO/H₂ mixture with a flow rate of ca. 5 l/hr using a D-500 Siemens diffractometer with CuK α radiation and a HTK-10 Anton Paar thermo-chamber. The scanning rate was 0.5° 2 θ /min. A diffraction region of 2 θ = 85°-95° was chosen because it contained the peaks of the initial and reduced

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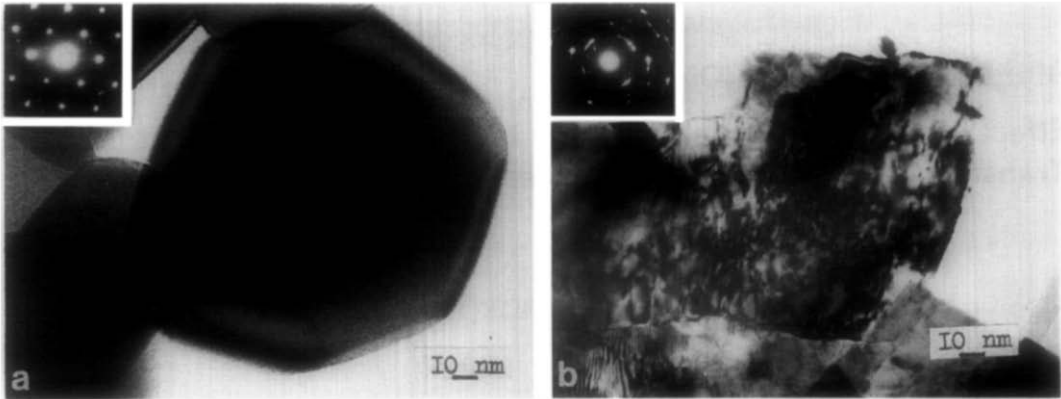


FIG. 1. Micrographs of NiO(I) (a) and NiO(II) (b) specimens. Selected-area electron diffraction patterns are shown in the insets.

phases, namely, (400) NiO, (311) Ni, and (112) Ni₃C. The (511) peak of Ge, being used as internal standard, was also situated here. The scan began immediately after the defi-

nite temperature was reached. It takes about 25 min to collect each diffraction pattern. Transmission electron microscopy (TEM) was performed using a JEM-100CX ma-

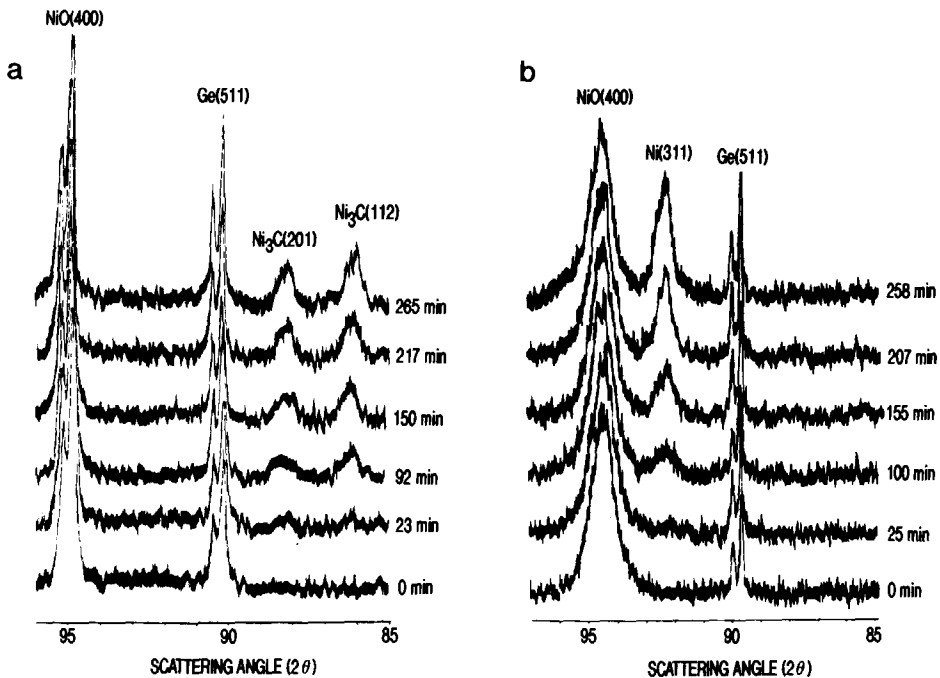


FIG. 2. X-ray diffraction patterns obtained during *in situ* reduction of samples of NiO(I) (a) and NiO(II) (b).

chine (resolution limit 3 Å, accelerating potential 100 kV).

3. Results and Discussion

TEM has revealed that NiO(I) particles have the form of thin platelets (Fig. 1a); the most developed (111) plane, as evident from a selected-area electron diffraction pattern, is shown in the inset Fig. 1a. Microcrystals of the NiO(II) specimen subjected to (SD + HP) treatment are characterized by a well-developed dislocation network (see Fig. 1b). The concentration of lattice defects is so high that the "monocrystal" structure of the NiO particle is transformed into a "polycrystal" structure (see the ring diffraction pattern in the inset to Fig. 1b).

X-ray diffraction patterns for both NiO specimens during reduction are given in Figs. 2a and 2b. Ni₃C was a new phase identified by XRD in the NiO(I) specimen about 45 min after the beginning of the experiment. The amount of the carbide phase increased slowly in the CO/H₂ reducing mixture. After 4.5 hr ca. 32% of the initial NiO was transformed into Ni₃C.

In contrast with the above results under the same conditions (i.e., at 240°C in a flowing CO/H₂ mixture), the loaded NiO(II) specimen was reduced to metallic nickel. It takes nearly 50 min to form the metallic phase. Only 21% of bulk NiO was transformed after the long experimental procedure (about 5 hr).

Thus, we have observed that under reduction two different phases are formed (Ni₃C and Ni) depending on the microstructure of

the initial NiO. Indeed, the possibility of nickel carbide formation from NiO(I) particles with the most developed (111) plane is great because there is a structural similarity between the (111) plane of NiO and the (0001) plane of Ni₃C. An increase in the dislocation density of the 'loaded' NiO specimen may result in the appearance of a great number of unsaturated Ni atoms in the vicinity of dislocation outlets on the (111) plane. The disordered surface structure of the close packed plane in the loaded NiO(II) particle has no structural similarity with the (0001) plane of Ni₃C. Thus, NiO(II) is transformed into metallic Ni more easily than into Ni₃C.

Thus, our data indicate that structure similarity plays a significant role in NiO structure transformation when treated with a CO/H₂ mixture. A detailed description of the *in situ* reduction process will be given in a forthcoming publication.

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