Controlled Reduction of NiO Using Reactive Ball Milling under Hydrogen Atmosphere Leading to Ni−NiO Nanocomposites

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Received July 22, 2004. Revised Manuscript Received September 7, 2004

Controlled mechanochemical reduction of NiO has been carried out by room-temperature ball milling under H_2 atmosphere. During the milling, a gradual conversion of NiO into Ni occurs, with no intermediate phases being formed. The amount of Ni and its crystallite size can be tuned by the ball-milling parameters, leading to the formation of Ni−NiO (metal−oxide) nanocomposites. The initial microstructure of the NiO powder is shown to play an important role in the reduction rate and on the final microstructure of the nanocomposites formed. The results indicate that the mechanically induced defects have a strong influence on the kinetics of the reduction process.

Introduction

The reduction of NiO ($NiO + H_2 \rightarrow Ni + H_2O$) is a reaction with high important technological significance, not only as a source of Ni from Ni ores but also due to its importance in catalytic reactions.[1,2] From the basic point of view, the reduction of NiO is regarded as a model reaction due to its single-stage transformation.[2] Moreover, metal−oxide nanocomposites (containing NiO and/or Ni) are receiving increased attention not only for their interesting chemical characteristics, such as catalysts,[3] fuel cell electrodes,[4] gas sensors,[5] or supercapacitors/battery hybrids[6] but also for their magnetic properties since NiO is antiferromagnetic and Ni ferromagnetic.[7−9] In addition, metal−ceramic materials are also interesting since they typically exhibit enhanced mechanical properties.[10] The methods usually employed for the reduction process are based on high-temperature treatments under H_2 atmosphere.[11,12] These studies show that the reaction is strongly influenced by the concentration of defects, in particular oxygen vacancies, in the starting material. It is noteworthy that the use of controlled high-temperature H_2 reduction of mixed oxides to form metal−oxide nanocomposites has been reported.[13,14] However, the temperature and H_2 pressure conditions to achieve the desired nanostructure can be critical in many cases.[13]

In this paper we show that partial reduction of NiO can be achieved by reactive ball milling under hydrogen atmosphere, leading to the formation of Ni/NiO nanocomposites. Mechanical milling is a well-known technique, largely used in a wide range of processes. In mechanical treatments carried out by ball-milling, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the balls and the powder. The high concentration of defects and the continuous interfaces renewal, associated with the milling-induced enhanced atomic mobility, promote different phenomena depending on the materials being milled. For example, the extension of the solid solubility

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10.1021/cm048810n CCC: $27.50

limits, the production of intermetallic compounds with crystallite sizes at the nanometer scale, or the synthesis of novel crystalline and amorphous materials have been reported.[15] The properties of the resulting material depend on the large number of parameters involved in the milling process: (i) the intrinsic nature of the initial materials together with their mechanical properties, chemical constitution, and structural properties; (ii) the parameters of the ball-milling process itself, such as ball to powder weight ratio (BPR), milling time, rotational speed, and type of motion of the vials; and (iii) finally, the milling medium, i.e., the material of the balls and vials and the milling atmosphere.[15]

In the present study we demonstrate that ball milling of NiO powder under H_2 atmosphere is a suitable method to activate the reduction process that leads to the formation of Ni. The influence of the different milling parameters on the reaction mechanism and the microstructure of the final products is investigated. It is shown that the initial microstructure of the NiO powders and the steel milling medium play a crucial role on the reduction process.

Experimental Section

High-purity NiO powders[16] were milled at room temperature under H_2 (6 bar) or Ar (1 bar) atmosphere, in a planetary ball mill (Fritsch Pulverizette 5), using a frequency of 300 rpm. Modified stainless steel vials, to allow milling under different gas atmosphere, together with stainless steel balls (12 mm in diameter) were employed. Note that, for comparison, milling of NiO was also performed in agate vials and balls, under Ar atmosphere. The milling intensity was tuned by changing the ball to powder mass ratio (BPR), from 3:1 to 18:1, leading to a milling power range of 5.3−31.9 W. A complete description of the procedure utilized to calculate the energy involved in the process is reported in refs 17 and 18. The milling intensity is defined as follows:

$$I = E_k f$$

where E_k is the kinetic energy transferred at each collision ($E_k = (1/2)mV_c^2$, m is the mass of the ball and V_c the collision speed of the ball) and f is the number of collisions per second. The total energy transferred per unit mass of powder, the *specific dose* (D_M), is then defined as follows:[19]

$$D_M = It/m_p$$

where t is the milling time and m_p the mass of the powder. The necessary corrections to the impact energy, as described in ref 20, were also taken into account.

To study the influence of the milling parameters on the reduction process, different types of milling experiments were performed, (i) at the same milling intensity (21.3 W) varying the milling time (2, 4, 6, 8, or 12 h) and (ii) at different milling intensities (5.3, 10.6, 21.3, or 31.9 W) for a constant milling time of 8 h. In addition, the influence of defects of the initial NiO on the reduction process was investigated by performing premilling of NiO powder under Ar atmosphere for different times (2, 4, 8, or 12 h) and subsequently milling in H_2 atmosphere for the same time (8 h) at 21.3 W milling intensity.

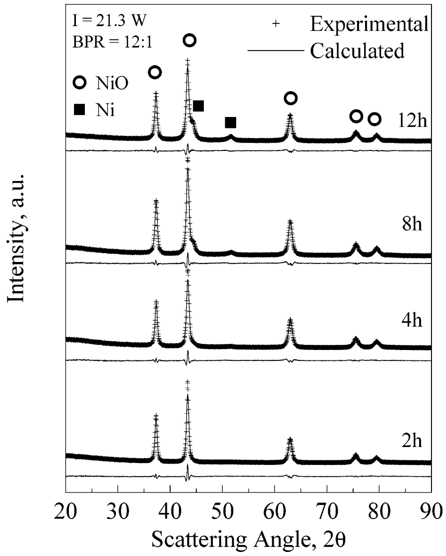

Figure 1. X-ray diffraction patterns of the NiO powder milled for 2, 4, 8, and 12 h in H_2 atmosphere at a 12:1 BPR. The profiles calculated from the fitting procedure are displayed as a continuous line while the symbols (+) are the experimental points. The error calculated by the difference between the experimental and the fitted plot is also shown at the bottom of each pattern.

Transmission electron microscopy (TEM) observations were carried out in a JEOL JEM 100CXII microscope, operating at 100 keV. The powders were prepared by gluing them on TEM grids with M-Bond 610 glue and subsequently thinning the sample by ion milling.

X-ray diffraction (XRD) was performed in the 10−120° range on the as-milled samples with a Philips 3050 diffractometer using Cu K_α radiation. The analysis of the diffraction patterns was carried out with a fitting program based on the Rietveld full pattern fitting method.[21] This quantitative analysis provides information about the phases and phase percentages, the crystallite sizes, and the lattice microstrains. The structure parameters such as lattice constants are determined with an accuracy at the worst of 1/1000. In other parameters, such as microstructure parameters (crystallite size or microstrains), which are very correlated between them, the error is larger, i.e., of the order of 10%, including the approximations involved in assuming a Voight function as a model for the observed line profile broadening. The quantitative Rietveld procedure is sufficiently reliable to differenciate 1−2% of each phase from sample to sample. The residual weight factor, R_{wp}, which is a useful indicator for the goodness of the fit was in any case below 7%.

Results and Discussion

Evolution of the Reduction Reaction. *(1) Milling at Constant Intensity: Effect of the Milling Time.* Figure 1 shows the XRD patterns, together with the calculated profiles, obtained from the Rietveld analysis, of the samples milled for 2, 4, 8, and 12 h (with a BPR of 12:1, I = 21.3 W). The errors resulting from the fitting procedure, calculated as the difference between the experimental and the calculated profiles, are also shown. As can be seen, the small errors clearly testify of a very good agreement level. The figure shows that, for the sample obtained after 2 h of milling, the diffraction peaks of fcc. NiO dominate in the pattern, and the Ni features are hardly visible. However, after

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Table 1. Summary of the Microstructural Parameters of Ni and NiO Obtained from the Fitting Procedure on NiO Powder Milled for 2, 4, 8, and 12 h in H_2 Atmosphere at a 12:1 BPR

milling time (h)	dose (kJ/g)	a_{NiO} (nm)	$\langle D \rangle_{NiO}$ (nm)	wt % NiO	a_{Ni} (nm)	$\langle D \rangle_{Ni}$ (nm)	wt % Ni
0		0.4177(0)	>100	100			
2	30.643	0.4177(0)	44	98.3	0.3543(1)	7	1.6
4	61.286	0.4177(0)	38.7	93.9	0.3543(0)	10.1	4.2
6	91.929	0.4177(1)	35	92.7	0.3543(0)	12.6	5.9
8	122.573	0.4176(5)	31.4	88.8	0.3541(9)	12.9	9.5
12	183.859	0.4175(8)	27	82.6	0.3540(2)	12.9	15.4

4 h, a small peak at $2\theta = 44.5°$, corresponding to Ni, starts to appear. By increasing the milling time, the structure of fcc, Ni becomes increasingly more pronounced (additional peaks at $2\theta = 52°$ and $2\theta = 92°$), attesting to the continuous increase of the amount of Ni formed. After 12 h of milling, the Ni formation is clear.

A summary of the microstructural parameters of Ni and NiO obtained from the fitting procedure on NiO powder milled for 2, 4, 8, and 12 h in H_2 atmosphere at a 12:1 BPR is shown in Table 1. The refinement analysis of the diffraction profiles evidences that a contraction of the NiO elementary unit cell occurs when increasing the milling time, from 0.4177(0) nm for unmilled NiO to 0.4175(8) nm after 12 h of milling. The introduction of defects in the NiO lattice as well the formation of oxygen vacancies contribute to this behavior. On the other hand, the lattice parameter of the Ni formed is found to be slightly larger than the tabulated value, decreasing with milling time from a value of 0.3543(1) to 0.3540(2) nm. The high strain level, due to the mechanical action[22,23] and some residual oxygen or H incorporated in the Ni matrix could explain this effect. Indeed, relatively large microstrain values are obtained from the Rietveld refinements after long-term milling, of around 0.003 for NiO and 0.004 for Ni. Interestingly, as can be seen in Figure 2, the NiO and the Ni crystallite sizes show opposite behaviors with milling time: while the crystallite size of the NiO, $\langle D \rangle_{NiO}$, decreases continuously with milling time, the Ni crystallite size, $\langle D \rangle_{Ni}$, is found to increase for short milling times (e.g., $\langle D \rangle_{Ni} \sim 7$ nm after milling for 2 h), tending to level off for milling times longer than 6 h ($\langle D \rangle_{Ni} \sim 12.5$ nm). The evolution of the NiO crystallite size with milling time is the one expected from a brittle material subjected to repeated mechanical impact.[15] The milling-time dependence of $\langle D \rangle_{Ni}$ is more striking. In fact, two competitive effects take place simultaneously: on one hand, the milling tends to reduce the crystallite size, while, on the other hand, the Ni nanocrystals progressively form and grow during the milling, due to the continuous reduction of NiO. Even by doubling the milling time (6 vs 12 h), the crystallite size of Ni remains constant, clearly testifying that a balance between the milling effect and the metal formation process has been reached.

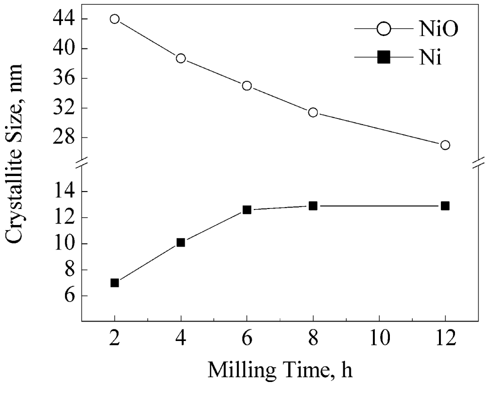

Figure 2. Dependence of the crystallite size of NiO and Ni on milling time. The lines are guides to the eye.

(2) Milling at Different Intensities: Effect of the Ball to Powder Mass Ratio. Different samples, with a BPR of 3:1, 6:1, 12:1, and 18:1, corresponding to the milling intensities of 5.3, 10.6, 21.3, and 31.9 W, respectively, were prepared. The hydrogen pressure (6 bar), the rotational speed (300 rpm), and the milling time (8 h) were kept constant. As can be seen in the corresponding XRD patterns displayed in Figure 3, no Ni was produced for the lowest intensity (5.3 W). This indicates that the energy transferred to the powder during milling is not high enough to initiate the reaction. For higher milling intensities the Ni peaks become clearly visible. A summary of the microstructural parameters of Ni and NiO obtained from the fitting procedure on NiO powder milled in H_2 atmosphere with a BPR of 3:1, 6:1, 12:1, and 18:1, for a constant time of 8 h, is shown in Table 2. The Rietveld refinements reveal that the NiO lattice parameter and the NiO crystallite size decrease, whereas the Ni crystallite size increases when the milling intensity is increased. This indicates that the effect of increasing the milling time while keeping constant the milling intensity is analogous to increasing the milling

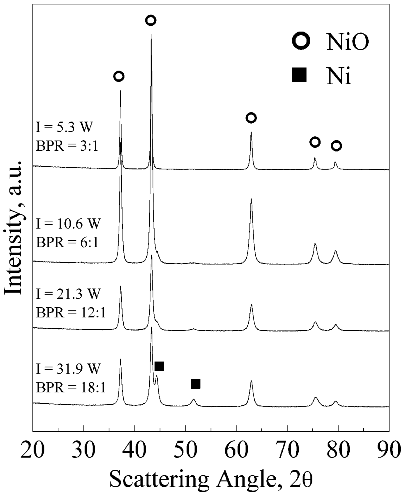

Figure 3. XRD patterns of the samples obtained with a BPR of 3:1, 6:1, 12:1, and 18:1, corresponding to intensities 5.3, 10.6, 21.3, and 31.9 W, respectively, for a constant milling time of 8 h.

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Table 2. Summary of the Microstructural Parameters of Ni and NiO Obtained from the Fitting Procedure on NiO Powder Milled in H_2 Atmosphere with a BPR of 3:1, 6:1, 12:1, and 18:1, for a Constant Time of 8 h

BPR	dose (kJ/g)	a_{NiO} (nm)	$\langle D\rangle_{NiO}$ (nm)	wt % NiO	a_{Ni} (nm)	$\langle D\rangle_{Ni}$ (nm)	wt % Ni
3:1	30.643	0.4177(4)	65.3	100			0
6:1	61.286	0.4177(2)	37.9	95.8	0.3544(5)	10.6	2.6
12:1	122.572	0.4176(1)	31.7	89.5	0.3541(9)	12.7	9.1
18:1	183.859	0.4175(7)	25.4	77.1	0.3539(4)	16.8	20.5

intensity keeping constant the milling time and hence that the structural changes induced on the powders depend on the total energy transferred during the milling. This can be clearly seen in Figure 4, where the percentages of Ni obtained from both studies, i.e. by changing the milling time at constant intensity (BPR 12:1) and varying the intensity at the same milling time (8 h), are plotted both as a function of the specific dose, i.e. the total milling energy per gram of powder. The values for both processes fall roughly on the same curve, indicating that both routes are equivalent. These results agree with what is found in the case of the amorphization reaction between transition metals by ball milling.[19] Namely, the milling regime does not influence the reaction pathway but only the transformation rate, consequently the reduction process is isokinetic as a function of D_M. As can be seen in the figure, the percentage of obtained Ni extrapolates to zero at about a milling energy of 25 kJ/g. Hence, a threshold energy exists to start the reduction process. In the case of the sample milled at constant intensity (21.3 W), corresponding to a BPR 12:1, this minimum energy is equivalent to an induction time of about 50 min. This pseudoinduction time corresponds probably to a mechanical energy storage time during which no metallic Ni is formed, but O vacancies are created. This hypothesis is supported by the progressive contraction of the NiO lattice with milling.

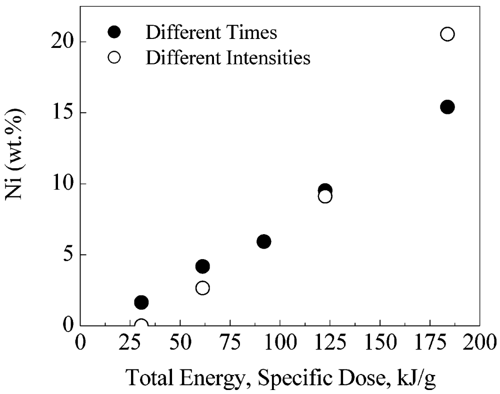

Figure 4. Ni percentages for the samples milled at constant intensity (BPR 12:1) for different times (●) and at different intensities (○) for the same time (8 h) as a function of the total energy transferred to the powders during milling.

(3) Role of the Initial NiO Microstructure. Previous studies on high-temperature reduction of NiO under hydrogen have demonstrated that the defects in NiO play an important role in the reduction process, particularly in the dissociation rate of hydrogen.[2,24,25] To further investigate the role of the powder microstructure on the reduction process, the following study was carried out: the powder was premilled under Ar atmosphere during 2, 4, 8, and 12 h. Subsequently, the different premilled powders were additionally milled for 8 h under H_2 atmosphere.

Shown in Figure 5 are the X-ray patterns of the samples obtained by different premilling times in Ar. As can be seen in the inset of Figure 5, the amount of Ni formed increases with premilling. For example without premilling a Ni weight percentage of about 9% is obtained, while for the sample premilled for 12 h the amount of Ni increases to ~29 wt %. These results confirm that the kinetics of the reduction process is strongly influenced by the initial NiO microstructure, evidencing the fundamental role of the concentration of defects in the initial powders.

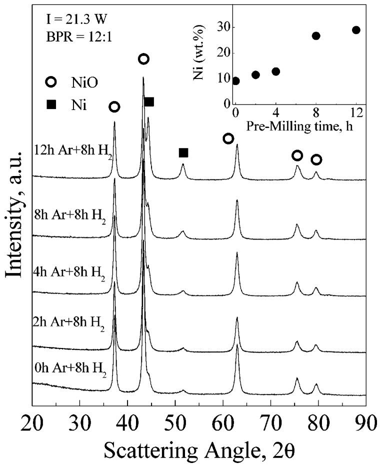

Figure 5. X-ray diffraction patterns of the NiO powder premilled for 0, 2, 4, 8, and 12 h and subsequently milled 8 h under hydrogen atmosphere (I = 21.3 W). Shown in the inset is the dependence of the Ni percentage on the premilling time.

Note that the main effect of premilling on the NiO powders is to reduce the crystallite size from larger than 100 nm (unmilled) to 20.6 nm (premilled 12 h), although the microstrains increase with the premilling from lower than 0.0008 (unmilled) to 0.002 (premilled 12 h). Moreover, it should be noted that after milling under Ar for 4, 8, and 12 h, small broad halos can be observed at 2θ positions close to the ones of Ni. The amount of this phase (which could be considered as a kind of "disordered Ni") is not more than 3 wt %. This formation of disordered Ni during the premilling, and possibly during the H_2 milling, can act as nucleation sites for the dissociation of H_2, hence aiding the reduction process. It could be argued that the formation of this phase could result from the fact that the milling may create a large number of O vacancies, which could subsequently favor the diffusion of Ni atoms. When a sufficient amount of Ni atoms is accumulated, they might nucleate forming Ni clusters, which could be detectable by XRD. Nevertheless, this possibility has

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been ruled out by the results of milling NiO in Ar with an *agate* medium, where no Ni was formed, although the milling conditions were adjusted to have approximately the same milling energy as when milling in steel. In fact, when milling in steel, due to the presence of Fe and Cr in the vials and balls, a displacement reaction could occur. Namely, some of the O of the NiO can be transferred to the Fe and Cr forming iron oxide and chromium oxide and consequently producing metallic Ni. Nevertheless the XRD spectra did not show the characteristic features of iron or chromium oxides, although the quantitative analysis of the XRD spectra yields a value of up to ~2% of metallic bcc iron (probably debris from the steel vials and balls due to mechanical abrasion). However, the Fe and Cr oxidation could take place at the surface of the vials and balls. Note that since the Gibbs free energies of formation of Cr_2O_3 and Fe_2O_3 are much larger than that of NiO ($\Delta G(\mathrm{NiO}) = -216$ kJ/mol, $\Delta G(\mathrm{Fe_2O_3}) = -740$ kJ/mol, $\Delta G(\mathrm{Cr_2O_3}) = -1000$ kJ/mol [26]), the *solid-state* reductions $2Fe + 3NiO \rightarrow Fe_2O_3 + 3Ni$ or $2Cr + 3NiO \rightarrow Cr_2O_3 + 3Ni$ are thermodynamically favored. Moreover, this displacement reaction hypothesis is largely supported by recent studies[27-29] on thin films in which the interface between NiO and Fe was shown to result in a reduced Ni layer and an oxidized Fe layer at the interface. Indeed, in a recent study, Luches et al.[27] have pointed out the oxidation−reduction reactions that have taken place at the interface of thin Fe films (1−10 monolayers) deposited onto a NiO film, even with a deposition of iron conducted at room temperature.

Microstructure. The bright-field and dark-field (from the (200) Ni ring) TEM images of the sample premilled for 12 h in Ar and subsequently milled for 8 h in H_2 as shown in Figure 6a and 6b, respectively. It can be seen that the as-milled powders consist of composites, in which nanoparticles corresponding to metallic Ni are embedded in a NiO matrix. It can also be observed from the dark-field image that the Ni particles exhibit a range of sizes, from a few nanometers to tens of nanometers. In some of these nanocomposites, the Ni tends to be located at the edges of the larger NiO particles. Moreover, sometimes, a core−shell structure is observed (see Figure 6c). This could be an indication that the reduction process of NiO starts at the surface of the NiO particles. The microstructure for other milling conditions is similar, although the amount of Ni nanoparticles and the size distribution changes, with more Ni and large Ni particles with higher specific dose, consistent with XRD results.

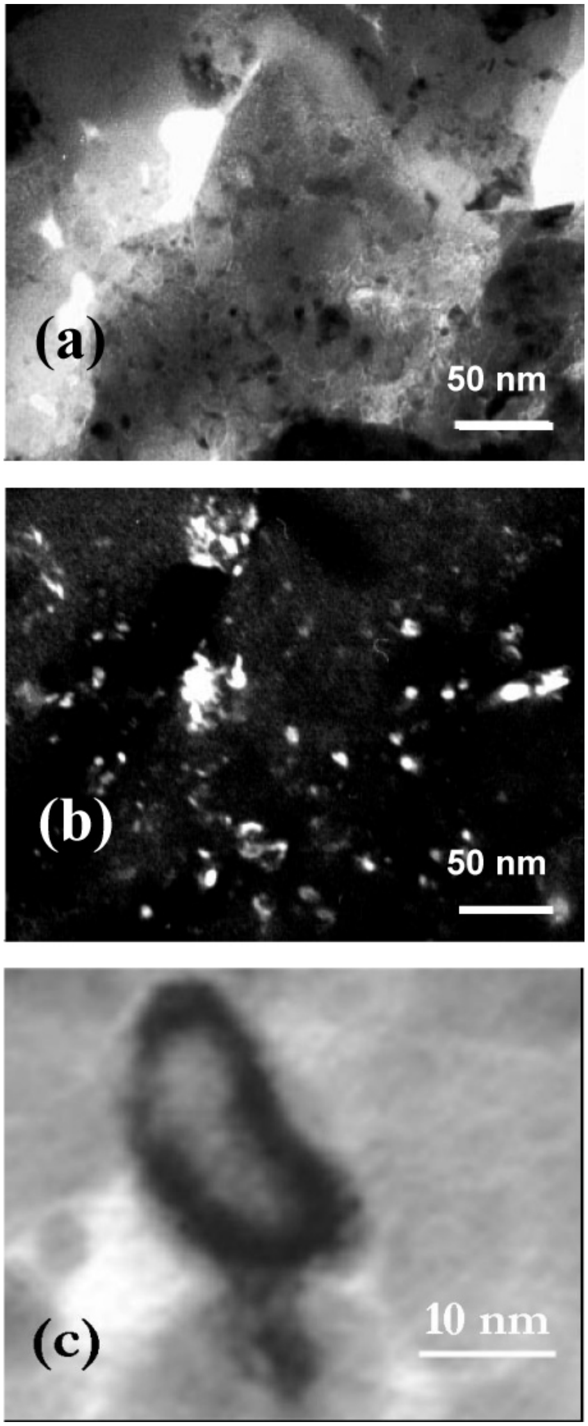

Figure 6. TEM micrographs of the sample premilled for 12 h in Ar and subsequently milled for 8 h in H_2: (a) bright-field, (b) dark-field, and (c) enlargement of a bright-field image showing a representative core−shell structure.

Reduction at High Temperatures vs Mechanochemical Reduction. The reduction process of NiO under hydrogen by high-temperature treatments has been extensively studied.[25,30-32] However, a direct correlation between the studies of NiO reduction on perfectly crystalline, well-oriented surfaces conducted by temperature treatments and the reduction of NiO powder by ball milling is difficult to establish. Nevertheless, the general conclusions of reducing at high temperatures can be applied, to some extent, to understand the results obtained in this study.

The reduction process by temperature treatment has been described in terms of a five-step mechanism:

First of all, the hydrogen is dissociated at the NiO surface in the first stages of the reaction. This is often

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referred to as the induction period, during which no metallic Ni is created. The time span of the induction period is largely affected by temperature (with increasing temperatures, the induction time decreases and/or disappears) and by defects (for the more defective surfaces, the induction time is shorter).

Diffusion of the hydrogen atoms toward reactive centers occurs.

The Ni−O bonds are broken, producing metallic Ni atoms.

These Ni atoms nucleate to form metallic aggregates.

Finally, the growth of Ni crystallites occurs. The hydrogen dissociation takes place on the created Ni surface. This is known as "autocatalytic effect", so the reduction rates increase proportionally with the formed Ni surface area.

From this mechanism, additional observations and conclusions have been drawn:

The reduction reaction takes place at the interface between the oxide and the reduced Ni. The limited diffusion of the hydrogen atoms into the Ni layer and of the slow outward diffusion of the water molecules produced during the reduction are responsible for the decreased rate observed in the final stages of the reaction.

Added water partial pressure to the hydrogen reduces the reaction rate and extends the induction period.

No intermediate phase was observed, i.e., the transformation of NiO into Ni is direct.

Additionally, attempts to understand the role of the defects in the reduction have been carried out by creating defects on single-crystal surfaces by Ar^+ sputtering[33] and the NiO reduction under hydrogen has been also studied on particles with nanocrystalline grain size.[24,25]

In our study, the reduction of NiO under hydrogen is carried out by ball milling at room temperature. Although the main role of the milling is to generate highly defective structures presenting dislocations, vacancies, stacking faults, and a high density of grain boundaries, the overall reduction process should follow the same steps as those described above. Similar to the NiO reduction at high temperatures, in our case, where the NiO reduction is mainly mechanically induced, a minimum milling time, which depends on the milling intensity, is also required in order to start the formation of Ni, i.e., to activate the reaction. Moreover, we also observe a growth of the Ni crystallite size for increasing milling times. Therefore, the reduction mechanism seems to consist also of first a nucleation of small Ni crystallites, followed by the subsequent growth of the nucleated crystallites. It can be argued that O-vacancies are created by the mechanical action, thus, probably, the hydrogen may be directly dissociated by the Ni atoms present at the surface (catalytic effect). Additionally, the diffusion of hydrogen is largely facilitated by a high density of grain boundaries generated during milling. Actually, the diffusion distances are constantly reduced, due to the decrease of the NiO crystallite size during milling. Moreover, it has to be taken into account that during milling the increase in local temperature due to the impact between the powders and the balls[15] could also assist the reaction. Similarly to high-temperature reduction, defects also accelerate the reduction process.

Conclusion

In summary, we have demonstrated that Ni can be formed controllably by partial reduction of NiO upon reactive ball milling, leading to Ni−NiO nanocomposites. The reduction rate is found to depend linearly on the total energy transferred to the powder during milling. A threshold mechanochemical energy is necessary to start the reaction corresponding to an induction time in which a critical concentration of defects is stored in the system. The induction time depends on the milling conditions. Moreover, we have pointed out the role of the microstructural properties of the powder on the reduction rate, showing that the amount of obtained Ni is related to the degree of disorder in the initial NiO powder. Additionally, the formation of disordered Ni during the milling, due to the reducing effects of the milling medium (steel vials and balls), can also assist in the H_2 reduction of NiO.

Acknowledgment. V.L. and J.S. acknowledge the NEXBIAS Project (HPRN-CT 2002-00296) for its support. J.N. thanks A. Llobet for stimulating discussions. Partial financial support from 2001-SGR-00189 and MAT-2004-01679 projects is also acknowledged.

CM048810N

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