Lattice Parameter, Microstrains and Non-Stoichiometry in NiO. Comparison between Mosaic Microcrystals and Quasi-Perfect Single Microcrystals

BY F. FIEVET
Laboratoire de Chimie des Matériaux Divisés, Université Paris 7, 2 place Jussieu, 75221 Paris CEDEX 05, France

P. GERMI AND F. DE BERGEVIN
Laboratoire de Cristallographie, CNRS, 166 X, 38042 Grenoble CEDEX, France

AND M. FIGLARZ
Laboratoire de Chimie des Solides Pulvéruents, Université de Picardie, 33 rue Saint Leu, 80039 Amiens CEDEX, France

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Abstract

Twelve samples of three kinds of highly divided nickel oxide, prepared from nickel hydroxide at low temperature, have been compared from the double point of view of mean lattice parameter variation (uniform strain) and lattice microstrains (non-uniform strain). These samples are black non-stoichiometric NiO with a mosaic texture, a green stoichiometric NiO with the same mosaic texture and black non-stoichiometric NiO made up of tiny quasi-perfect single crystals (monolithic NiO). The textures of the three kinds of oxides have been inferred from electron microscopy and diffraction and X-ray diffraction. Crystallite sizes and microstrain values have been obtained from X-ray line broadening analysis. Deviations from stoichiometry have been obtained from chemical analysis. Correlations between uniform strain, non-uniform strain, texture and stoichiometry have been researched. It appears from the comparison of the results that uniform and non-uniform strains are insensitive to the extent of deviation from stoichiometry. The non-uniform strain is mainly due to the mosaic texture of the grains. The uniform strain related to the mean lattice parameter variation appears to be related to the small crystallite size. These two aspects are related to the mechanism of the oxide formation from the hydroxide.

Introduction

In a previous paper (Fiévet, Germi, de Bergevin, Roger & Figlarz, 1976) it was shown that finely divided NiO samples, obtained from Ni(OH)$_2$ in an oxidizing atmosphere, exhibit an increase in the pseudo-cubic lattice constant and a high microstrain value by comparison with a bulk oxide. It has been shown too, that the electron microscopy, electron diffraction and X-ray diffraction results obtained from these samples are consistent with a model assuming a mosaic texture for each grain of the powder, i.e. each grain, which appears from selected-area electron diffraction as a single crystal, is, in fact, built up of a large number of tiny crystallites slightly misoriented. Although some experimental evidence of such a mosaic texture has been reported, for example subgrains in metals and alloys or mosaic blocks in NaCl crystals (Renninger, 1934), this mosaic model is usually considered 'as a highly over-simplified concept since imperfections in a crystal may be the result of dislocations and inhomogeneous strains without any clear cut subdivision into mosaic blocks', (Warren, 1969, p. 331; see also Hirsch, 1956). Nevertheless, this simple model with small-angle boundaries which subdivide the grains into small coherent crystallites will appear in this study very suitable to describe our samples. This model implies that the dislocations which produce the subdivision into crystallites produce a non-uniform strain within the crystallites as has been effectively observed.

Two different factors may be considered a priori to account for the observed variation of the lattice parameter and of microstrains: first the surface-volume ratio of the sample which is related to the texture of the sample, namely to its porosity and to its crystallite size, and second the departure from stoichiometry.

In the previous study (Fiévet et al., 1976), these two factors vary simultaneously. As illustrated in Fig. 1, the lattice parameter variation may be correlated with $1/L_m$, the inverse of the mean crystallite size, which is a measurement of the surface-volume ratio. It may be correlated with the $\text{Ni}^{3+}/\text{Ni}_{\text{tot}}$ ratio as well, which is a measure of the departure from stoichiometry. Finally, it may also be correlated with the microstrain coefficient $\varepsilon$. In order to determine the main cause of the observed parameter increase, two other types of NiO samples have been investigated in the present paper.

In order to evaluate the influence of the non-stoichiometry, a nickel oxide with a similar surface-
volume ratio and a similar mosaic texture but with an almost stoichiometric composition has been prepared in argon. For convenience this sample will be called NiO(mos., st.) and the previously studied NiO will appear as NiO(mos., non-st.) in the following text.

In order to investigate the influence of the mosaic texture it has been necessary to prepare finely divided NiO samples formed of quasi-perfect single crystals. In other words, each grain of a sample of this series, even the most divided sample, may be considered as a single crystallite. We call such a grain a monolithic grain (Figlarz, Vincent, Lecaille & Amiel, 1967) and these samples will appear as NiO(monol., non-st.).

Experimental methods

Preparation and characterization of the oxides

(1) NiO(mos., non-st.). The conditions of preparation have been described in detail elsewhere (Fiévet et al., 1976). They can be summarized briefly as follows. The starting material is well crystallized Ni(HOH)₂ (Fig. 2a). This powdery hydroxide is heated in an air flow and then maintained at a constant temperature between 473 and 673 K. In that temperature range the oxide particles retain the habit of the starting material (Fig. 2b–d), but they become finely porous, with an increasing pore size as the final temperature rises. A selected-area electron diffraction pattern obtained on one particle (Fig. 3a, b), clearly shows that each particle may be considered as a single crystal lying on the (111) plane. However, the size of these single crystals observed by electron microscopy is by no means consistent with the crystallite size inferred from X-ray line broadening. Typically, the grain size of the sample shown in Fig. 2(b), inferred from electron microscopy, is several thousand Ångströms the thickness is several hundred Ångströms. The corresponding crystallite size is 145 Å. This difference in magnitude between grain size and crystallite size, the electron diffraction pattern of a single crystal obtained with one grain and the dark field image of such a grain obtained with a 220 spot (Fig. 3c) support the choice of the mosaic model to describe these samples.

Owing to the oxidizing atmosphere of preparation, these samples are black non-stoichiometric oxides Ni₁₋ₓO, electro-neutrality being maintained by Ni³⁺ ions. The amount of Ni³⁺ was measured in an inert atmosphere by iodometric titration after the sample had been dissolved in a hydrochloric acid solution. The total amount of nickel was determined by a complexometric method and by atomic absorption. The
ratio Ni$^{3+}$/Ni$_{\text{tot}}$ is a measurement of the deviation from stoichiometry. The results for NiO(mos., non-st.) samples are given in Table 1.

(2) NiO(mos., st.). The starting material is the same Ni(OH)$_2$ as above. The dehydration is carried out in a purified argon atmosphere free from oxygen with a rising temperature rate of 5 K per hour up to 553 K. The oxide is kept at this final temperature for 70 h. The yellow–green colour of the sample is related to an almost stoichiometric composition (El Shobaky, Gravelle, Teichner, Trambouze & Turlier, 1967). This oxide is not stable in air and it blackens in a few seconds. In order to use conveniently standard X-ray diffraction procedure the oxide particles must be stabilized for a limited period of time. This has been achieved by a method involving the polymerization of a monomer on

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO(mos., non-st.)</th>
<th>NiO(mos., st.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_s$ (Å)</td>
<td>$d_s$ (Å)</td>
<td>$d_{\text{av}}$ (Å)</td>
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<td>24</td>
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<td>215</td>
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Table 1. Crystallite size, lattice parameter and its relative variation from bulk, microstrain value and deviation from stoichiometry for different NiO samples.

Fig. 3. (a), (b) An isolated platelet of a highly divided NiO(mos., non-st.) and its electron diffraction pattern. (c) The dark field image of the same platelet obtained from a 220 spot.
the surface, which results in encapsulation in a plastic film (Robbins, Swisher, Gladstone & Sherwood, 1970). At first the oxide was recovered in situ with a deaerated solution of diethylene glycol dimethacrylate in acetone (dilution monomer to acetone 1:2). Then acetone was removed by heating and the monomer-coated particles were suspended in mineral oil. The slurry was vigorously stirred and heated to 373 K for four hours in order to achieve polymerization. All these operations were conducted in purified argon atmosphere. After this, the sample can be put in air and excess mineral oil is removed by washing with hexane. The final product has a pale green colour, and does not show a noticeable blackening after standing in air for ten hours. One cannot measure a noticeable amount of Ni$^{3+}$ by the chemical analysis method described above, which means that the ratio Ni$^{3+}$/Ni$_{tot}$ is certainly less than 0.1 x 10$^{-2}$.

Moreover, as may be inferred from electron microscopy (Fig. 4), this sample has the same mosaic texture as NiO(mos., non-st.). Therefore this sample may be considered as a mosaic, stoichiometric, finely divided nickel oxide, NiO(mos., st.).

(3) NiO(monol., non-st.). It is possible to obtain small, quasi-perfect single crystals of NiO from nickel hydroxy carbonate, probably because it is a poorly crystallized material. We have preferred to use as starting material a turbostratic nickel hydroxide, i.e. a hydrated nickel hydroxide formed by parallel and equidistant layers similar to those found in well crystallized Ni(OH)$_2$ but with layers randomly oriented and separated by intercalar water molecules which join them (Le Bihan & Figlarz, 1972). This hydroxide appeared by electron microscopy as aggregates of thin, crumpled sheets without any definite shape (Fig. 5a). Because of this habit of the grains and the disordered structure we thought that this material would be very suitable for providing finely divided monolithic NiO samples. Moreover its dehydration temperature is lower than the decomposition temperature of nickel hydroxy carbonate and so it is possible to obtain very small grains.

Monolithic oxide samples have therefore been prepared by heating turbostratic hydroxide in air at a rising temperature rate of 5 K per hour up to a final temperature varying from 473 to 673 K. The resulting oxide was maintained at this final temperature for several hours. The most divided oxide, obtained at 488 K (Fig. 5b), is made up of very tiny crystals randomly oriented as can be seen from the electron diffraction pattern (Fig. 5c). The size of the crystals increases as the preparation temperature rises (Fig. 5d, e). The crystallite size obtained from X-ray line broadening (Table 1) is roughly corroborated by the evaluation of the grain size on electron microscopy photographs (Fig. 5b, d, e). Therefore each grain may be considered as a crystallite which diffracts coherently, i.e. as a monolithic grain.

The black colour of these samples and the oxidizing atmosphere of the preparation indicate that the oxide is non-stoichiometric; a value for Ni$^{3+}$/Ni$_{tot}$ of 3.1 x 10$^{-2}$ is found for the most divided sample of this series, NiO(monol., non-st.).

(4) Bulk NiO. A sintered NiO sample was prepared in air at 1273 K. This oxide has been considered as...
a reference sample with the bulk lattice parameter $a_0 = 4.177 \, \text{Å}$, a lattice free of microstrains and a composition very close to the stoichiometric one.

**X-ray diffraction**

The samples have been studied by reflexion with a goniometer ($\theta$–$2\theta$) with Cu Kα radiation. The sample was placed in a vacuum to avoid air scattering. The horizontal divergence of the beam was 0.015 rad; Soller slits placed in the direct beam limit the vertical divergence to 0.013 rad. Beyond the sample, the monochromator height limits this divergence to 0.035 rad. The receiving slit width was 0.5 mm (0.002 rad).

Line intensities were measured by step scanning in the range 13–68° $\theta$. The step was 0.01° $\theta$ and the counting time was 10 s.

Systematic errors due to the drifting of the zero and to displacement of the sample have been inferred from the cast shadow of the sample at $\theta = 0^\circ$.

The centroids of the lines have been calculated. For very broad lines the estimation of the background is not easy: it has been evaluated from the variance range function method of Langford (1968).

**Results**

**Lattice constant**

NiO has a rhombohedral structure with $a = 2.9520 \pm 0.0003 \, \text{Å}$ and $c = 60^\circ 4.5'$ at 295 K (Toussaint, 1971). Such an $c$ value is very close to the value $c = 60^\circ$ of the primitive rhombohedral cell of a f.c.c. lattice. The lattice may be considered as a slightly distorted f.c.c. lattice with a small contraction along one of the threefold axes. At room temperature, with the restriction that high-angle lines are not considered, the structure appears as pseudo-cubic with $a = 4.1769 \, \text{Å}$ for the cubic cell (ASTM powder diffraction file no. 4-835). Because of the breadth of the lines it has not been possible in the study of our finely divided nickel oxides to take into account the small rhombohedral distortion and we have compared the pseudo-cubic lattice constant $a_m$ of our samples. By ignoring the distortion we make a relative error smaller than $10^{-6}$ because when a line is split into several components by a rhombohedral distortion, the centroid of all the components does not depend on the first order of the distortion angle but only on the second order, whereas it depends on the first order of the pseudo-cubic parameter value.

The results for the three kinds of samples are given in Table 1. $a_m$ is a mean value obtained from the centroids of $n$ lines ($n = 9$); an extrapolation towards $\theta = 90^\circ$ does not seem to improve the reliability of the results. The numbers in brackets in the table are the standard deviation of the mean value $a_m$ calculated by $\left[ \sum (a_i - a_m)^2 / (n(n-1)) \right]^{1/2}$ according to Cruickshank (1959). The degree of division of the different samples has been characterized by the crystallite size $L_m$; in Fig. 6 we report the variation of $a_m$ with crystallite size.

The NiO(mos., non-st.) series shows a continuous increasing deviation from the bulk oxide lattice parameter as the crystallite size decreases. This relative deviation $(a_m - a_0) / a_0$ reaches $4 \times 10^{-3}$ for the most finely divided sample of the series, $a_0$ being the lattice constant of the bulk sample.

The NiO(mos., st.) sample shows a behaviour very similar to that of NiO(mos., non-st.) (Fig. 6, Table 1). Although only one sample has been studied it appears that the increase in the lattice constant is not mainly due to the increase of deviation from stoichiometric composition: the main factor is actually the high degree of division of the material.

The NiO(monol., non-st.) samples also show such an increase of the lattice constant for small crystallites but the phenomenon seems to be a little smaller than for NiO(mos., non-st.) (Fig. 6, Table 1).

![Fig. 6. Variation of the lattice parameter with the crystallite size for NiO(mos., non-st.) (+), NiO(mos., st.) (o) and NiO(monol., non-st.) (•).](image)

![Fig. 7. $B \cos \theta = f(2 \sin \theta)$ curves for NiO(mos., non-st.) as the preparation temperature increases: (a) 478 K, (b) 493 K, (c) 523 K, (d) 558 K, (e) 628 K, (f) 673 K.](image)
Crystallite size and microstrains from line broadening

It has been shown previously (Fiévet et al., 1976) by the Williamson & Hall (1953) method that for NiO(mos., non-st.) samples, microstrains and crystallite size contribute together to the broadening of the X-ray diffraction lines. For a given sample, the plots $B \cos \theta = f(2 \sin \theta)$ fall on a straight line (Fig. 7). $B$ is the angular width at half maximum intensity of the line corrected, by the method of Klug & Alexander (1974), for the instrumental width measured on a bulk sample.

From the intercept, $B_0$, of the straight line, the mean crystallite size $L_m$ may be inferred from the equation $L_m = K^2 / B_0$, where $K$ is a dimensionless number known as the Scherrer constant. In a recent review Langford & Wilson (1978) recalled that, in accurate studies of crystallite size and shape, $K$ must be considered as depending on the $[hkl]$ direction and on the crystallite shape. In our case, we can use the mean value $K = 0.94$ proposed by Warren (1969, pp. 253–254) because:

1. the linearity of the curves $B \cos \theta$ versus $2 \sin \theta$ obtained for NiO(mos., non-st.) and for NiO(mos., st.) indicates that the crystallites are very isotropic in shape;
2. we focus our interest on the comparison between the samples rather than on absolute values of sizes.

From the slope of the straight line, the microstrains value $\epsilon = (\langle \delta \lambda \rangle / \delta)$ may be inferred. This coefficient $\epsilon$ is always greater than the root-mean-square strain, $\langle \epsilon^2 \rangle^{1/2}$, obtained from a Warren & Averbach (1950, 1952) treatment. Such a calculation, which gives simultaneously the mean square of the strains and the crystallite size distribution, would be very useful in the investigation of these samples. Unfortunately, we have encountered some difficulties in obtaining reliable results with our types of samples. We are trying now to solve this problem. Moraweck, Renouprez & Imelik (1973) have studied the crystallite size distribution in foliated nickel oxide samples by Fourier analysis of X-ray diffraction lines and small-angle scattering. They did not notice the contribution of strains to the line broadening. There is a large difference in the particle habit between our samples and those of Morawek, Renouprez & Imelik (1973) (the ratio of the thickness of the particles is about ten) which does not allow a very significant comparison between the results of X-ray line analysis.

In the present study we have estimated the $\epsilon$ coefficients by supposing that all the broadening effects give rise to a Cauchy profile. This choice can be justified by the two following remarks:

1. the curves giving the variance function versus the angular range, used to determine a correct background value, converge rapidly towards a straight line, which corresponds to a Cauchy asymptotic profile;
2. Williamson & Hall (1953) have shown that the plots $B \cos \theta$ versus $2 \sin \theta$ should be curved instead of straight lines if the broadening functions were of the Gaussian instead of Cauchy form; we actually observe straight lines at least for NiO(mos., non-st.) and NiO(mos., st.) samples.

Results for NiO(mos., non-st.) samples are given in Fig. 7 and Table 1. For this series the crystallite size decreases from 415 to 95 Å as the strains increase from $2.4 \times 10^{-3}$ to $16.8 \times 10^{-3}$.

The NiO(mos., st.) sample has the same crystallite size as the comparable sample of the NiO(mos., non-st.) series: 145 Å. The strain values $\epsilon$ are very similar for these two samples (Table 1, Fig. 8): $12.9 \times 10^{-3}$ and $12.7 \times 10^{-3}$, respectively. It may be concluded that deviation from stoichiometric composition and strains observed in mosaic NiO are not related.

![Fig. 8. $B(2\theta) \cos \theta \times 10^3$ curves for NiO(mos., non-st.), NiO(mos., st.) and NiO(monol., non-st.). The three samples have about the same crystallite size: 145, 145 and 110 Å respectively.](image)

![Fig. 9. $B(2\theta) \cos \theta \times 10^3$ curves for NiO(monol., non-st.) as the preparation temperature increases: (a) 488 K, (b) 538 K, (c) 643 K.](image)
The uniform strain is related to the small crystallite size and texture and so are almost negligible in monolithic oxide. The non-uniform strains are mainly due to the mosaic character of the final product. In fact a close topotaxic orientation and a mosaic texture in the final product are correlated as may be explained by the following scheme of the reaction mechanism. In the early stage of the decomposition there is always a topotaxic relationship between the starting and final products, the mismatch of the lattices inducing a strain. In the final product this strain, as the reaction proceeds, is either partly relieved by the formation of small slightly misoriented crystallites or is almost completely relieved by the splitting of the particles. As illustrated by other reactions (Guénot, Fiévet-Vincent & Figlarz, 1977), the formation of a mosaic crystal requires at the end of the reaction a close topotaxic orientation in the final product.

From this point of view one can compare the dehydration reaction of well crystallized Ni(OH)$_2$ and of turbostratic nickel hydroxide. In the former case, the topotaxic relations (00.1)Ni(OH)$_2$//(111) NiO and (110) Ni(OH)$_2$//(110) NiO are observed by selected-area electron diffraction (Fiévet & Figlarz, 1974) and a high value for $\varepsilon$ is obtained for samples prepared at low temperature, i.e. with a small crystallite size and with a high porosity. Subsequently, a further increase of temperature induces a development of the texture of the platelets which retain the same hexagonal habit with an increase of the crystallite size and a decrease of the porosity. This reordering allows a subsequent relief of the strains and then these samples exhibit a decreasing value of $\varepsilon$. In the case of the dehydration of the turbostratic hydroxide the reaction proceeds by a splitting of the crumpled sheets which allows an almost complete relief of the strains and then a small value of $\varepsilon$ is observed even for highly divided samples.

**Variation of lattice parameter**

The measured increase in lattice parameter may be explained by the small size of the crystallites rather than by the deviation from non-stoichiometry. Lattice parameter studies of thin films and small particles have been the subject of several works on various materials. Lafourcade & Larroque (1957) found a decrease in lattice parameter for small crystallites in thin films of gold and silver. Vergand (1975) reported the same observation on thin films of rare-earth metals. Wasserman & Vermaak (1970) also found a decrease in lattice parameter of small particles of gold and silver. In all these works the phenomenon is interpreted in terms of surface tension considerations. Conversely, an increase in lattice spacing of (100) planes has been observed as the thickness of the film decreases in (100) oriented thin films (Vook, Parker & Wright, 1967); a similar increase has been noticed in (111) planes of (111) oriented gold films (Vook, Ouyang & Otooni, 1972); both with almost a fiber texture. These authors explained their results by an outward relaxation at crystal faces so that two or three interplanar spacings are appreciably distorted.

For ionic crystals Rymer (1957) has found an increase in lattice parameter for small crystals of LiF. This seems
to be a general trend for ionic crystals studied by X-ray methods (Anderson, 1968). In the particular case of MgO, Cimino, Porta & Valigl (1966) have found an increase in lattice parameter as the crystallite size decreases. This variation is ascribed to adsorbed water forming a layer of Mg(OH)₂ which induces a dilating strain. Our samples of finely divided NiO also retain adsorbed water molecules and adsorbed hydroxyl groups (Fiévet & Figlarz, 1975). Nevertheless, it must be emphasized that MgO can be rehydrated easily at room temperature whereas NiO, even in a high degree of division, cannot. Therefore, this last interpretation seems to us less convincing in the case of NiO, although it may not be completely ruled out. Lattice parameter increase is more likely a crystallite size effect explained qualitatively by the surface relaxation of an important fraction of the atoms. It remains that the deviation from stoichiometric composition, which distinguishes NiO from previously studied ionic microcrystals, does not seem to play a significant role in the lattice parameter increase. At this point, the question arises of the nature of this departure from stoichiometry observed in our samples. Is the whole lattice affected by the phenomenon or is there only chemisorbed oxygen on the surface? An answer to this question may be found by comparing the three following investigations of Ni³⁺ in finely divided NiO: Uchijima, Takahashi & Yoneda (1967); Gisquet (1968); Deren & Stoch (1970).

These studies qualitatively agree with the fact that the greater part of the excess oxygen is located in a thin superficial layer; nevertheless, a small part of the excess oxygen is incorporated in the lattice. Moreover, it must be emphasized that for crystallites of 50 and 100 Å, if a three-plane-thick layer is affected by a perturbation, a volume containing about 40 and 20%, respectively, of the total nickel ions is indeed affected. Therefore, in very finely divided samples, because of the high surface–volume ratio, one cannot neglect the possibility that surface phenomena affect bulk properties such as the lattice parameter.

In our case there is no relation between non-stoichiometry and lattice parameter variation because the influence of non-stoichiometry is probably low compared with the direct influence of the high surface–volume ratio.

Conclusion

All our results may be correctly explained by taking into account the surface effects related to the high surface–volume ratio and by assuming the validity of the mosaic model for the oxide grains. This mosaic model is also suggested by the mechanism of the nickel oxide preparation reaction involving close topotaxic relationships.

References