Experimental Study of Gases Occluded within Microscopic Cavities in Single Crystalline Nickel Oxide

R. FARHI,* G. PETOT-ERVAS,* C. PETOT,* G. DHALENNE,†
AND F. LE GUERN‡

*C.N.R.S., Laboratoire des Propriétés Mécaniques et Thermodynamiques des Matériaux, Université Paris-Nord, 93430 Villetaneuse, France, †Laboratoire de Chimie Appliquée, Université Paris-Sud, 91405 Orsay Cedex, France, and ‡Laboratoire de Volcanologie, Centre des Faibles Radioactivités, 91191 Gif-sur-Yvette Cedex, France

The existence of microcavities (1–10 μm) in single crystalline nickel oxide was demonstrated by microscopic observations, and their effect on electrical conductivity described elsewhere. It was proposed that the anomalous conductivity values could be attributed to the presence, within the cavities, of oxygen gas under high pressure. In order to confirm this assumption, Raman microprobe and gas-phase chromatography experiments have been performed on NiO single crystals. The results obtained concerning the gases detected (oxygen and nitrogen) are in qualitative and quantitative agreement with the microscopic observations and the electrical conductivity measurements.

I. Introduction

Observations performed on many single crystals of nickel oxide, using optical (1) as well as transmission electron microscopy (2), have demonstrated the existence of cavities whose maximum dimensions vary typically from 1 μm in diameter for zone melted single crystals to 10 to 20 μm for single crystals prepared using the Verneuil technique. The effect of the presence of such cavities on the properties of the single crystals, such as electrical conductivity and deviation from stoichiometry, in the intermediate temperature range (850–1123 K) has been studied previously (3). The main observations of this work concerned the influence of the sample history on the electrical properties at intermediate temperatures. Anomalously high values of the elec-

trical conductivity observed in initially prepared single crystals were attributed to the presence of molecular gaseous oxygen under high pressure within the cavities. Another finding concerned the consequence of thermal treatments, which result in extensively decreasing conductivity values. This last observation can be explained by a corresponding decrease in the oxygen partial pressure within the cavities.

In order to obtain semiquantitative results of oxygen pressures, two experimental methods have been used. The first one is a Raman microprobe technique referred to as MOLE (4), which gives *in situ* information about the nature and the relative quantities of gases occluded in cavities, but is limited to the detection of cavities greater than 5 μm. The second technique involves the milling of nickel oxide single

crystals in order to release the occluded gases which are then analyzed by gas-phase chromatography (5).

II. Raman Spectroscopy

Single crystals for the experiments were prepared using an arc-image furnace operating at 4 cm hr^{-1}, high growth rate resulting in cavities 5–10 μm in diameter, or by the Verneuil technique which gives larger cavities. Observations were made at first on samples polished with diamond paste, but this introduced microcleavage at the surface of the crystals, thereby permitting the occluded gases to escape. It was not possible to detect any gas in these samples and subsequent observations were made on unpolished cleaved crystals. A stream of argon gas was passed above the sample during the observation in order to avoid any interference with oxygen and nitrogen of air. The wavelength of the argon laser light used for the Raman study was 4880 or 5145 Å.

The Raman spectra obtained for each of the observed cavities exhibited peak frequencies at 2330 cm^{-1}, typical of the vibration of the N≡N triple bond, and 1556 cm^{-1}, which corresponds to the vibration of the oxygen molecule (Fig. 1). In no case could the existence of a very wide band between 1300 and 1600 cm^{-1} be avoided. It was verified that both peak frequencies were not observed when the laser beam was focused outside the cavity.

The differential cross sections of oxygen and nitrogen are similar so that the ratio of the areas under the peaks is approximately equal to the ratio of their partial pressures. The values of these ratios are reported in Table I for the different single crystals. The two results mentioned for sample 1 refer to two different cavities of a Verneuil single crystal.

The vibration frequencies of H–H and O–H bonds (respectively 4160 and 3650
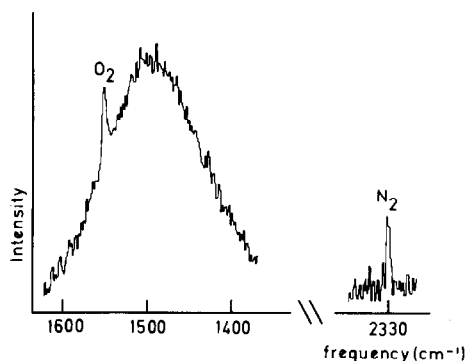

FIG. 1. Raman spectra obtained at wavelengths near 1550 cm^{-1} and 2350 cm^{-1}.

cm^{-1}) were not detected in any of the samples examined.

III. Gas-Phase Chromatography

a. Experimental Apparatus

The nickel oxide single crystals were crushed in a Fritsch crushing-mill, the balls and crucible of which were made of agate. The cap of the crucible was machined from hard stainless steel and was provided with three Pneurop vacuum flanges. One of these was connected to a primary vacuum pump, one to the six-way sampling valve of the chromatograph and the other to a tap by which inert gas can be introduced into the crucible, for example for the calibration. The whole apparatus is shown schematically in Fig. 2. The chromatograph used was an Intersmat IGC 112 M with an analysis column composed of a 5 Å molecular sieve, 2 m long, and a reference column made of Porapak. Both columns were maintained at a temperature of 338 K. The flow rate of

TABLE I

Sample	Growth technique	P_{O_2}/P_{N_2}
1	Verneuil	2.5
1	Verneuil	6
2	Arc-image furnace	1.2

helium used as carrier gas was approximately 30 ml mn^{-1} S.T.P.

The capacity of the crucible and tubes connecting it to the vacuum pump and to the chromatograph was measured by filling the whole apparatus with water and was found to be equal to 190 ± 2 cm^3. The capacity of the sampling loop of the six-way valve (Fig. 2) was approximately 0.5 cm^3 and was thus negligible when compared with the volume of the gases in the crucible.

b. Calibration

Accurate determinations of the quantities of gases released by the single crystals during the milling required a preliminary calibration of the apparatus, as indicated below. A small quantity of air contained in the crucible was injected into the analysis column, using the six-way sampling valve, and the corresponding oxygen and nitrogen peaks were recorded. The partial pressures of both gases were then reduced by exhausting air from the crucible until an absolute total pressure of about 0.2 atm was obtained. Afterward, helium was introduced in order to restore the total pressure to approximately 1 atm, and a small fraction of this new gas mixture was injected in the chromatograph. The intensities of the two peaks obtained corresponded to the new

FIG. 3. Calibration plots obtained for oxygen and nitrogen.

partial pressures, the values of which could be deduced from the residual vacuum in the crucible when the pumping ceased. The ratio P_{N_2}/P_{O_2} is presumed to remain constant during this pumping. These operations were repeated until the sensitivity limit of the chromatograph was reached. It was thus possible to plot the partial pressure values of each gas vs the area under the corresponding peaks. Straight line plots were obtained for both gases as shown in Fig. 3.

c. Nature and Amount of Occluded Gases

All the samples were analyzed using the same procedure as follows. A test was performed before each milling in order to confirm that the whole apparatus was airtight. The crucible was evacuated without a sample and after a blank milling for 10 min, a small fraction of the residual gases was injected into the chromatograph. No peaks were recorded under these conditions, i.e., the quantity of residual gases in the crucible is less than the detection level of the chromatograph. Pieces of single crystals with a total weight of about 20 g were then introduced into the crucible, the tightness of
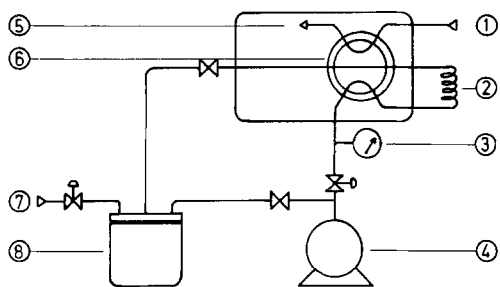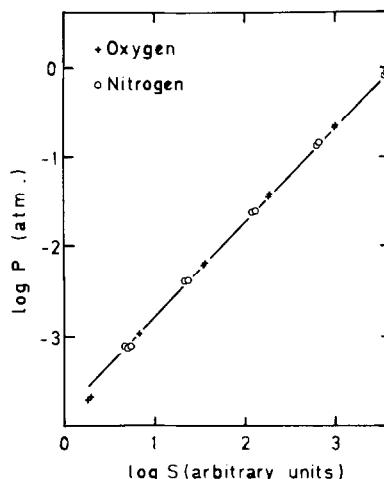
FIG. 2. Experimental apparatus for the analysis of occluded gases by milling and chromatography: (1) carrier gas inlet; (2) sampling loop; (3) manometer; (4) primary vacuum pump; (5) toward molecular sieve; (6) six-way sampling valve; (7) helium gas inlet used for the calibration; (8) crushing-mill.

which was further checked by sampling and measuring the residual gases after evacuating for 10 min. The crushing-mill was then started. Small quantities of released gases were injected into the chromatograph every 4 min during the milling process. The peak intensities for oxygen and nitrogen were found to increase asymptotically with time, and the milling was stopped when the heights of the peaks recorded for three successive injections were constant, usually 30 to 45 min after the start of the crushing-mill. The oxygen and nitrogen partial pressures in the crucible were then deduced from the calibration curves.

Three sets of different samples prepared using the Verneuil technique have been analyzed. The first two sets were not subjected to any thermal treatment, except the rather rapid cooling due to this technique of crystal growth. The third one was annealed under helium gas at 1473 K for 20 hr, and then rapidly cooled (100 K mn⁻¹). The results obtained are given in Table II.

Under the experimental conditions described in Section a, the retention times of oxygen and nitrogen were 80 and 170 sec, respectively. An example of the peaks obtained for set No. 2 is given in Fig. 4. No other gas was detected from the samples studied when using this method.

d. Interpretation of the Results

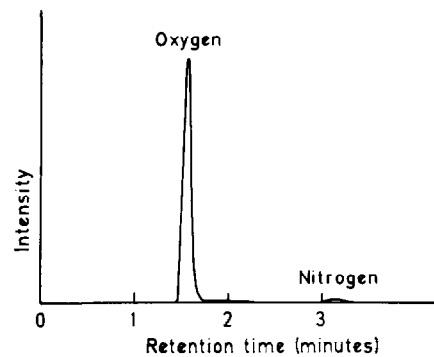One of the aims of this work was to obtain quantitative information about the

FIG. 4. Peaks observed for occluded oxygen and nitrogen for set No. 2 (Table III).

pressures of the gases within the microcavities existing in the nickel oxide single crystals. It is thus necessary to know the volume occupied by these cavities for each of the samples. Since the temperature rise due to the milling is negligible, the ideal gas law can be applied:

$$P_{\text{crucible}} \cdot V_{\text{crucible}} = P_{\text{cavities}} \cdot V_{\text{cavities}}$$

In this relation, P_{crucible} denotes the partial pressure of the gas in the crucible at the end of the milling (Table II), V_{crucible} is the net capacity of the crucible and its connections (190 ± 2 cm³), P_{cavities} is the partial pressure of the gas in the cavities at room temperature, and V_{cavities} the total volume occupied by the cavities. An estimation of this last quantity is rather difficult, because the cavities which can be observed by optical microscopy are always larger than 5000 Å. Smaller cavities seem to be less nu-

TABLE II

Set number	Samples weight (g)	Milling duration (min)	Oxygen partial pressure (atm)	Nitrogen partial pressure (atm)
1	27.14	37	$(8.4 \pm 0.9)10^{-4}$	$(5.6 \pm 1.2)10^{-4}$
2	24.02	45	$(6.6 \pm 0.3)10^{-4}$	$(1.5 \pm 0.1)10^{-4}$
3[a]	17.21	33	$(6.5 \pm 5.3)10^{-5}$	$(3.1 \pm 1.4)10^{-4}$

[a] Heat treatment of 20 hr at 1473 K under helium gas.

TABLE III

Set number	Oxygen partial pressure (atm)	Nitrogen partial pressure (atm)
1	39 ± 4	26 ± 6
2	348 ± 16	8 ± 1
3[a]	5 ± 4	23 ± 10

[a] Heat treatment of 20 hr at 1473 K under helium gas.

merous, but it is not possible to neglect their volume completely. On the other hand, the number of cavities per cubic centimeter can vary by a factor of five, from one region of the crystal to another, for arc-image furnace samples. Nevertheless, the numerous density of cavities measurements performed by ourselves and other authors (1, 2) permit an estimation of their relative volume. In Verneuil as well as in arc-image furnace samples, this value is about 10^{-3} cm³/cm³ of crystal. The partial pressure values can thus be calculated and are given in Table III.

IV. Discussion of the Results

Only nitrogen and oxygen were detected in each sample. The observation of hydrogen is practically impossible when helium is used as the carrier gas in the chromatograph, but hydrogen was also not detected during the Raman microprobe experiments. The different flames used during the growth of Verneuil crystals were always oxidizing, and this could be the reason why hydrogen was not detected. Water vapor was not observed either by the chromatography technique or by the Raman experiments.

The results reported in Table III concerning set No. 1 are in agreement with the semiquantitative results obtained by the Raman technique (Table I). On the other hand, the comparison of the results obtained for sample sets No. 1 and 2 shows that the growth conditions seem to play a

prevalent role in the generation of gas pressures within the cavities. These two sets of samples did not undergo any special thermal treatment and they differ only in the conditions of preparation (growth rate, initial powder mesh, degree of oxidation of the flame, etc.). These results are to be compared with those obtained previously using electrical conductivity measurements at intermediate temperatures (3): the oxygen pressure values of 39 and 348 atm calculated at room temperature for the nonannealed crystals are in fairly good agreement with those of 200 and 1000 atm deduced from the electrical conductivity measurements made at a temperature three times greater.

Concerning the sample set No. 3 in Table III, the results obtained are in qualitative agreement with these last measurements: the annealing of a single crystal under conditions of oxygen pressure and temperature giving rise to a small departure from stoichiometry results in a significant decrease in the electrical conductivity value (3, 6), which is attributable to the quasi-total removal of oxygen from the cavities through the surface of the sample. Moreover, Table III shows that the nitrogen partial pressure is not modified during the annealing. This result can be easily explained since nitrogen is not involved in the thermodynamic processes giving rise to the deviation from stoichiometry of the oxide crystal.

The existence of nitrogen gas within the cavities can be explained by the difference in solubility of this gas in the solid and liquid phases of the oxide. When solidification occurs, the excess nitrogen dissolved in the liquid phase is rejected and this results in the formation of cavities in the solid containing the gas under pressures which can be relatively high.

Concerning oxygen, an additional phenomenon, which can be the prevailing one, has to be taken into account together with the preceding mechanism. The cooling

down of a nonstoichiometric oxide at a constant oxygen partial pressure is accompanied by a decrease in the deviation from stoichiometry, when the enthalpy of formation of point defects is positive. For a sufficiently rapid cooling of the crystal, the corresponding excess of oxygen will be rejected within the cavities, rather than at the surface, because these represent the nearest solid–gas interfaces. This effect leads to an increase of the oxygen partial pressure in the cavities (3). This ejection of oxygen, which can induce a change in orientation and morphology of the cavities (1, 7), may give rise to oxygen partial pressures greater than for nitrogen within the cavities, though this increase can also be explained by a difference in the variation of the degree of solubility of both gases in liquid and solid phases.

Acknowledgments

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