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Deformation of NiO single crystals below room temperature: dislocation configurations

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NiO single crystals prepared by two crystal growth techniques (zone melting in an arc-image furnace and Verneuil crystallization have been deformed by compression along ⟨0 0 1⟩ at temperatures as low as 4.2 K, and the dislocation substructure observed by transmission electron microscopy. The Peierls mechanism has been suggested as the mechanism controlling the mechanical behaviour at the lower temperatures. The dislocations generated at cavities found in the zone-melted crystals may be responsible for the increase of the flow stress of these crystals compared with the Verneuil ones.

1. Introduction

In spite of their refractory properties, oxides with the rock-salt structure show remarkable plastic properties at low temperatures; CoO, as well as MgO, have been deformed down to 4.2 K [1, 2]. However, nickel oxide was found to be hardly plastic at 77 K [3]; experiments showed that crystals prepared by the Verneuil technique were definitely more ductile than those prepared by a zone melting technique, a situation which was not explained through lack of microstructural observations.

Detailed transmission electron microscopy (TEM) can be performed on rock-salt oxides which are radiation-resistant. Systematic studies were made on MgO [4] and NiO deformed above room temperature [5, 6], which have many similar dislocation arrangements, with extensive dipole formation. For CoO, dipoles were also observed after deformation at 4.2 K, but they were believed to be due to recovery by dislocation glide when the specimens were warmed up to room temperature, or possibly to even higher temperatures during ion-thinning [1]. Following a similar approach, we have extended the work to NiO single crystals, which were deformed down to 4.2 K and examined by TEM.

2. Experimental procedure

Materials and techniques were identical to those described in our previous papers [1, 3], except that we did not use a cold stage for the preparation of TEM foils.

Very briefly, specimens were prepared by two crystal growth techniques: zone melting in an arc-image furnace and Verneuil crystallization. The latter gives crystals with higher impurity contents than the former [7]. Before deformation, some specimens were annealed for 48 h at 1200 °C in an atmosphere with a low partial pressure of oxygen ($P_{O_2} \simeq 10^{-2}$ Pa). This heat treatment decreases the departure from stoichiometry of NiO and may change the ionization of impurities such as Fe and Mn [8].

Mechanical tests and TEM observations were performed by conventional procedures as described earlier [1, 3].

3. Mechanical data

Compression along ⟨0 0 1⟩, at constant strain rate, was performed on single crystals grown by Verneuil and by zone melting techniques. Typical stress–strain curves τ–ε (where τ is the shear stress resolved on the {1 1 0} glide plane) are displayed in Fig. 1. In spite of the large difference in temperature, the two curves are very similar; the deformation at 77 K was performed with NiO single crystals prepared by zone melting, which was found to give harder materials at 77 K than those prepared by the Verneuil method [3]. It is remarkable that Verneuil crystals can be strained at 4.2 K (Fig. 1), with no pre-deformation, under shear stresses of 90–100 MPa; $\tau/\mu \simeq 2 \times 10^{-3}$ where μ ($= 4.5 \times 10^{10}$ Pa below 200 K) is the elastic shear modulus. Successive deformations were also performed on the same crystals while cooling from 300 to 4.2 K; this gives a good representation of the variation of yield stress τ_c with temperature (Fig. 2).

Between 300 and 4.2 K, the increase in strength is more gradual for NiO (Fig. 2) than for CoO [1]. Annealing at low oxygen pressure tends to soften NiO (Fig. 2) especially at room temperature, as already reported [5, 8]; the softening can possibly be ascribed to the presence of residual impurities [7]. The difference in Fig. 2 is hardly larger than the scatter of experimental data [3]. This scatter seems to increase

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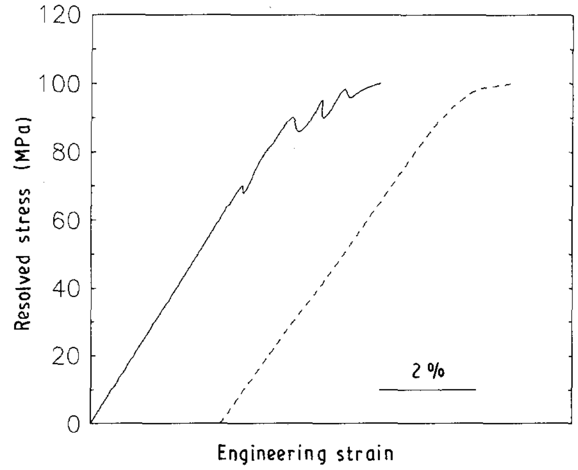

Figure 1 Deformation curves of resolved stress τ versus engineering strain ε for NiO compressed along ⟨0 0 1⟩ ($\dot{\varepsilon} = 10^{-5}\ s^{-1}$). (——) $T = 4.2$ K, Verneuil crystal annealed 48 h at 1200 °C and $P_{O_2} = 10^{-2}$ Pa. The drops in the τ–ε curve are probably due to crack propagation. (– – –) $T = 77$ K, zone-melted crystal.

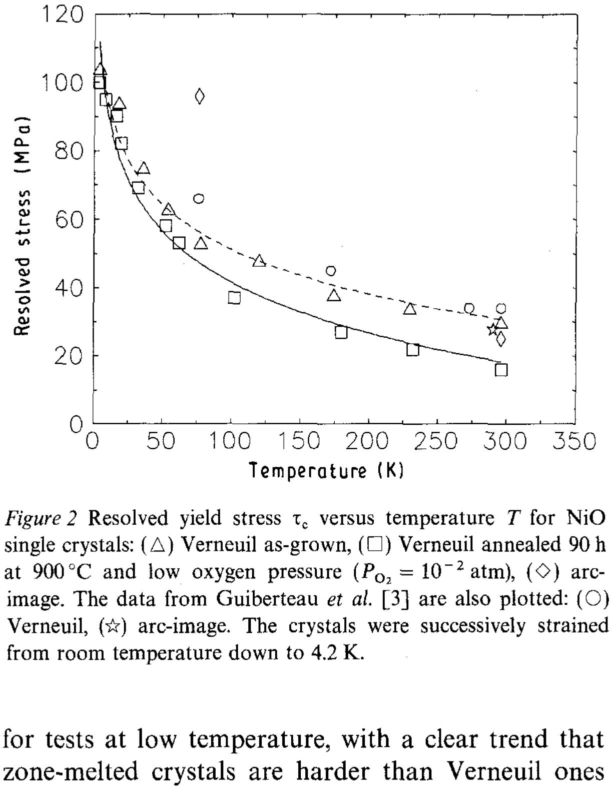

Figure 2 Resolved yield stress τ_c versus temperature T for NiO single crystals: (△) Verneuil as-grown, (□) Verneuil annealed 90 h at 900 °C and low oxygen pressure ($P_{O_2} = 10^{-2}$ atm), (◇) arc-image. The data from Guiberteau *et al.* [3] are also plotted: (○) Verneuil, (☆) arc-image. The crystals were successively strained from room temperature down to 4.2 K.

for tests at low temperature, with a clear trend that zone-melted crystals are harder than Verneuil ones (Fig. 2).

Apparent activation volumes V^* were determined from stress relaxations at each temperature step on Verneuil crystals, as-grown and heat-treated (Fig. 3). Similar values of V^* were found for both kinds of crystal below 100 K, the values being greater for annealed crystals above this temperature.

4. Microstructural observations

TEM with a Hitachi H800-2 microscope operating at 200 kV (Microscopy Service, University of Sevilla, Spain) was used to investigate dislocation structures in deformed specimens. Foils were cut a few degrees from a glide plane to identify the direction of the stress axis in the foil; furthermore, this avoided the brittleness of specimens deformed at 4.2 K.

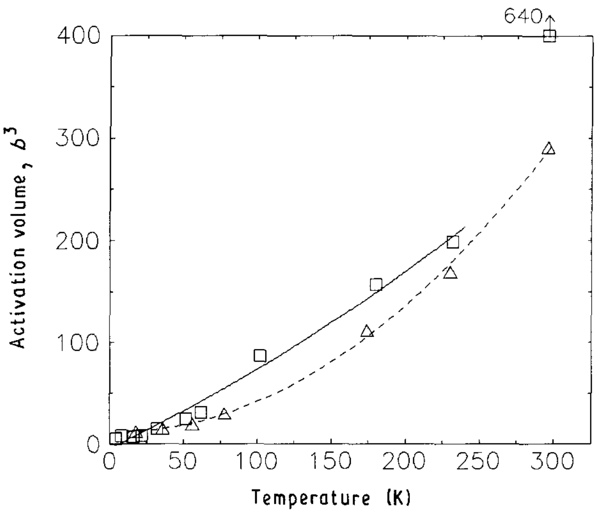

Figure 3 Apparent activation volume V^* (in b^3 units, $b = 0.296$ nm) versus temperature T for (△) as-grown and (□) annealed Verneuil NiO crystals.

A high density of polyhedral cavities ($\simeq 10^5\ mm^{-2}$) was observed by TEM in NiO prepared by zone melting, with sizes ranging between 200 and 300 nm (Fig. 4a and b). This is in agreement with the results of Dubois [9], who examined similar crystals by optical microscopy. For the Verneuil crystals, cavities were only rarely found in TEM (density of $\simeq 10^3\ mm^{-2}$), with diameters about 1 μm (Fig. 5).

In the Verneuil specimens deformed at 4.2 K, foils almost parallel to two orthogonal glide planes were observed. The density of dislocations was between 10^8 and $10^9\ cm^{-2}$. They were mostly dipoles and multipoles (Figs 5 and 6). Standard $\boldsymbol{g}\cdot\boldsymbol{b}$ analysis was used to check that the Burgers vectors were of $\frac{1}{2}$ ⟨1 0 1⟩ type, as in any f.c.c. crystal. The dipole separation was 17 ± 3 nm; this value was the average of the measured distances for micrographs obtained using $+\boldsymbol{g}$ and $-\boldsymbol{g}$ (with the deviation parameter s positive) diffraction conditions in a weak beam.

In isotropic elasticity, the maximum distance h between two dislocations in a stable dipole configuration is [10]

$$h = \frac{0.25\,b}{2\pi(1-\nu)}\left(\frac{\mu}{\tau}\right)$$

where $b = 0.296$ nm is the Burgers vector modulus, $\nu = 0.26$ (Voigt average) is Poisson's ratio and τ is the shear stress applied to dislocations. With $\tau = 100$ MPa (Fig. 2) one finds $h \simeq 70$ nm*, to be compared with 17 nm for TEM observations (Fig. 6). This gives an idea of the stress supported by dislocations during microstructure formation. It corresponds to 40 MPa, the flow stress value at 100 K (Fig. 2).

The dislocation lines lie along well-defined directions (Figs 5 and 6): (i) the [0 1 0] direction (edge

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*At $T \leq 200$ K, NiO is slightly anisotropic ($A \simeq 2.2$); the equilibrium distance derived from anisotropic elasticity [1] is close to 6 nm.

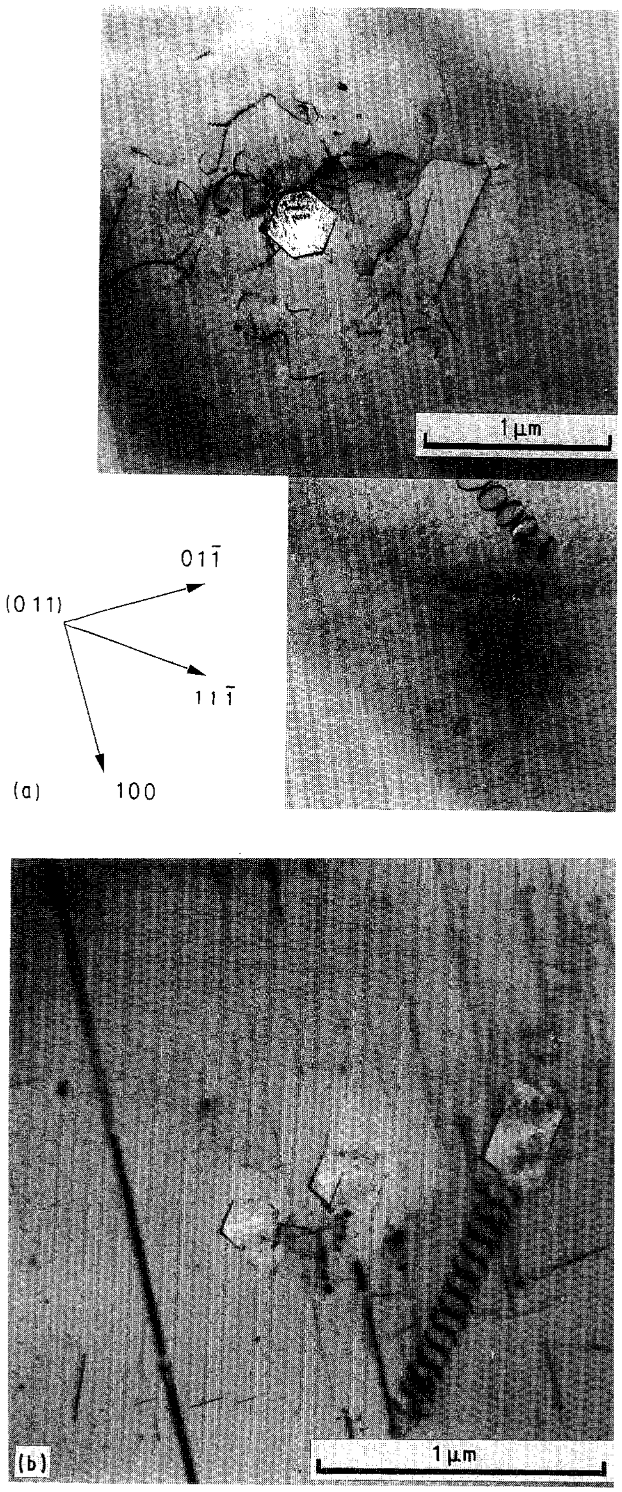

Figure 4(*a, b*) TEM micrographs of NiO grown by arc-image furnace technique deformed at 77 K, showing cavities surrounded by dislocations and strings of prismatic loops aligned along ⟨1 0 1⟩ (not in the foil plane). Edge dipoles are aligned along the [1 0 0] direction in (b).

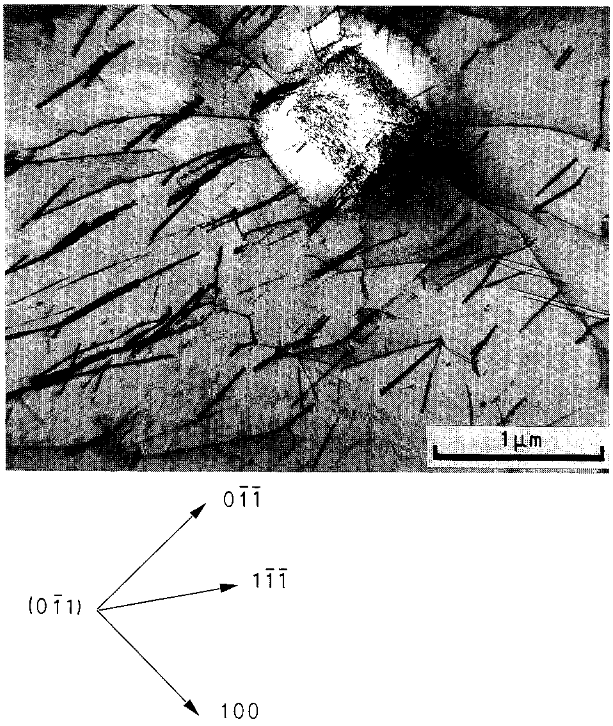

Figure 5 TEM micrograph of NiO grown by Verneuil technique deformed at 4.2 K, showing a cavity surrounded by dislocations.

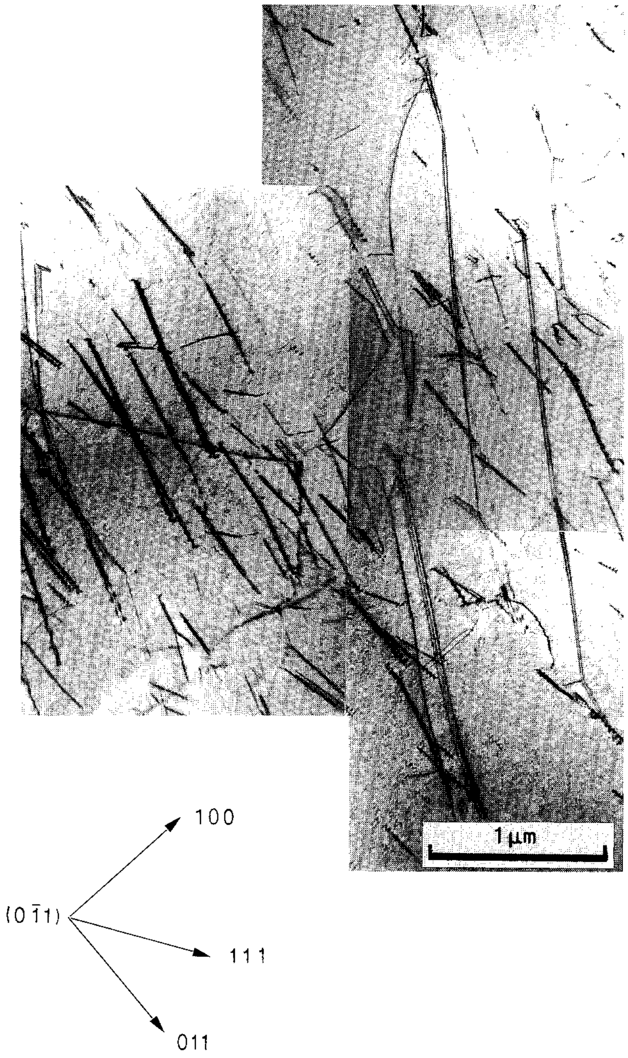

Figure 6 Array of dislocation dipoles and multipoles in Verneuil NiO deformed at 4.2 K.

character) which corresponds to the intersection of two orthogonal glide planes, and (ii) ⟨1 1 1⟩ directions (35° in character) which correspond to the intersections of a glide plane with the other two 60° glide planes.

After deformation at 77 K, we have mostly examined crystals grown by the zone melting technique. The substructure is dominated by two features:

(i) the cavities are surrounded by dislocations (Fig. 4a and b) accumulated during crystal growth or plas-

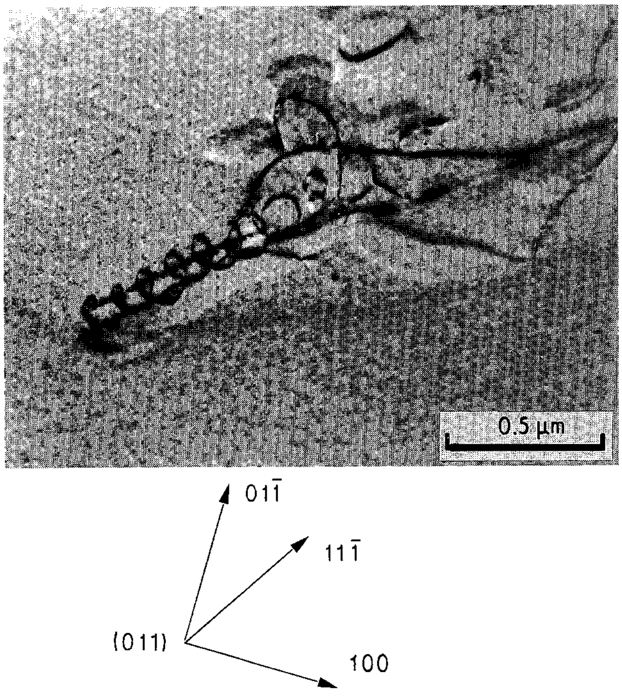

Figure 7 TEM micrograph of a helix formed by interaction between a string of loops and a dislocation. Zone-melted NiO crystal deformed at 77 K.

tic deformation. Dislocation loops aligned along ⟨1 1 0⟩ slip directions were observed near to cavities (Fig. 4a and b), sometimes with interactions with a dislocation (Fig. 7). These loops are prismatic, and seem to be punched out from cavities. Their diameters are between 150 and 200 nm, smaller than the sizes of the corresponding cavities.

(ii) long edge-dislocation dipoles were found along the [0 1 0] direction which is the intersection of two orthogonal activated planes (Fig. 4b). Their density is about 10^8 cm^{-2}. Their equilibrium distances are of the order of 20–30 nm, which corresponds to those calculated for $\tau = 35$–23 MPa. This indeed corresponds to the flow stress of crystals deformed at $T = 200$ K, implying significant recovery after the deformation at 77 K (Figs 1 and 2).

5. Discussion

5.1. Low-temperature deformation

Like other rock-salt structure oxides, NiO has been deformed at temperatures as low as 4.2 K (Figs 5 and 6). The dislocation substructure is typical of strained crystals with a large number of dipoles, as observed in deformed rock-salt structure compounds [4, 11]. We have shown that the distance between dislocations in dipoles agrees with that deduced from the flow at temperatures higher than for mechanical tests. This suggests that extensive recovery occurred after deformation at 4.2 K, when the specimens were warmed up to room temperature or higher during the preparation of thin foils for TEM. This conclusion is similar to that deduced from TEM observations of CoO deformed at 4.2 K [1].

The micrographs do not give indications concerning the obstacles to dislocation glide. We expect at 4.2 K a Peierls mechanism. In this situation, the deformation is controlled by the nucleation of kink pairs on dislocations. Following the analysis given earlier [1] for CoO, the maximum temperature T_c below which the Peierls mechanism operates is related to the activation energy H_o for kink pair formation at $\tau = 0$ by $H_o \simeq 30kT_c$ (k is the Boltzmann constant). At $\tau = 0$, this activation energy can be written

$$H_o \simeq a(a\,b\,\tau_p E_L)^{1/2}$$

where a is the period of the Peierls potential, τ_p the Peierls stress and E_L the line energy given by

$$E_L = \frac{Kb^2}{4\pi}\ln\left(\frac{R}{b}\right)$$

where R is the average distance between dislocations ($R \simeq 3000b$) and K the energy coefficient for dislocations, related to the elastic constants of the material ($c_{11} = 2.05 \times 10^{11}$, $c_{12} = 1.15 \times 10^{11}$ and $c_{44} = 1.10 \times 10^{11}$ Pa below 200 K [12]).

Using elastic anisotropy theory [10], the energy coefficients for screw and edge dislocations are: $K^{\text{screw}} = 7.0 \times 10^{10}$ Pa and $K^{\text{edge}} = 9.6 \times 10^{10}$ Pa. The ratio $K^{\text{edge}}/K^{\text{screw}}$ is 1.37, very similar to that found using isotropic theory [10] ($K^{\text{edge}}/K^{\text{screw}} = (1 - \nu)^{-1} = 1.35$). With these values and with $\tau_p \simeq 100$ MPa (Fig. 2), one can find $H_o^{\text{screw}} = 3.3 \times 10^{-20}$ J and $H_o^{\text{edge}} = 4.0 \times 10^{-20}$ J. The corresponding critical temperatures are $T_c^{\text{screw}} = 80$ K and $T_c^{\text{edge}} = 100$ K; the difference between the two values is so small that it renders the comparison with experiments uncertain.

From the experiment, only a crude estimate of T_c is possible because the Peierls region is narrow ($T \leq 40$ K); we deduce $T_c^{\text{exp}} \approx 120$ K or between 100 and 150 K, not lower than 100 K. This T_c^{exp} is close to the theoretical value of T_c^{edge}, not to T_c^{screw}, suggesting that the deformation is controlled by the motion of edge dislocations. This is opposite to our conclusion for CoO and to the general observations for NaCl structure crystals [10, 13, 14].

The two curves of Fig. 2 tend towards the same value, insensitive to heat treatments, at $T = 0$ K. Also, the activation volumes are of the order of b^3; they are about the same for the two heat treatments (Fig. 3). A Peierls mechanisms is obviously in agreement with these features.

5.2. Hardening mechanisms

The yield stress values for NiO single crystals are rather scattered at all temperatures [3]. At $T = 300$ K, Verneuil crystals seems to be harder than zone-melted ones; at $T = 77$ K the opposite was observed [3] (Fig. 2). We now attempt to rationalize these results.

Verneuil crystals have been found to have an impurity content larger than the zone-melted ones, giving a definite and distinct behaviour for plastic deformation at 1000–1100 °C [7]. This could account for a substantial fraction of the hardening and of the scatter of yield stress data around room temperature. In particular, annealing at different P_{O_2} values may lead to different states of impurity ionization and/or aggregation and, therefore, may explain the influence of

P_{O_2} on plastic behaviour (Figs 2 and 3), the purest specimens being less sensitive [8].

Some other mechanism must be invoked to explain the hardness of the purest crystals at $T = 77$ K (Fig. 3) [3]. This has to be correlated with the different contents of cavities and the associated dislocations.

Cavities have been observed in NiO single crystals prepared by the zone melting technique and their origins have been discussed by various authors [15, 16]. They can be surrounded by dislocation arrays in as-grown crystals [17]. However, alignments of prismatic loops have only been observed after deformation at $T = 77$ K. This is reminiscent of similar observations made around inclusions in AgCl [10]. Similar dislocation emissions were induced around internal discontinuities in LiF [18, 19], NaCl [19] and MgO [20] submitted to hydrostatic pressures. For NaCl and LiF, this has been found to enhance the flow stress of the crystals.

We have observed cavities and dislocation loop alignments in the zone-melted crystals (Figs 4 and 7); no such observation was made for Verneuil ones, which contain a small amount of cavities. This is very likely to be the origin of the large hardening of the first kind of crystal with respect to the second (Figs 1 and 2), the difference in impurity content having a minor role.

6. Conclusions

At high temperature, NiO Verneuil crystal plasticity is modified by the presence of impurities and the zone-melted crystals have been found to display an intrinsic behaviour [7]. However, the reverse is true at low temperatures; hardening by dislocations generated at cavities can be very efficient in increasing the flow stress of zone-melted crystals. Verneuil crystals allowed us to activate dislocation glide controlled by a Peierls mechanisms, in a limited range of temperature.

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