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Point defects and high temperature creep of NiO single crystals (*)

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Résumé. — Des monocristaux de NiO ont été comprimés par fluage entre 1 070 °C et 1 550 °C sous des contraintes comprises entre 10 MPa et 150 MPa. La pression partielle d'oxygène varie entre 10^{-5} atm. et l'air. Le fluage stationnaire semble dépendre de la concentration de lacunes d'oxygène $V_O^{\cdot\cdot}$, ce qui suggère un mécanisme de fluage dépendant de la diffusion de l'oxygène.

Abstract. — NiO single crystals have been crept in compression between 1 070 °C and 1 550 °C for stresses in the range 10 MPa-150 MPa. Oxygen partial pressures were varied between 10^{-5} atm. and air. The steady state creep rate seems to depend on the concentration of oxygen vacancies $V_O^{\cdot\cdot}$, in agreement with an oxygen diffusion controlled creep mechanism.

1. **Introduction.** — High temperature steady state creep is generally diffusion controlled. In oxides, it is accepted that the creep rate is related to the diffusion coefficient of the slowest species. However no experimental proof has been well established [1, 2]. Nonstoichiometric oxides provide good systems for studying the relation between diffusion and creep [2]. In a previous note, we have suggested that the creep rate $\dot{\varepsilon}_S$ of NiO single crystals is controlled by oxygen diffusion between 950 °C and 1 200 °C in air [3]. Activation energies for creep [3] and diffusion [4] have been found to be very similar. We have then extended our measurements to higher temperature ($T \lesssim 1\,500$ °C) (1 500 °C = 0.8 Tm) and various oxygen pressure (10^{-5} atm. $< P_{O_2} <$ 0.21 atm.; 1 atm. $\simeq 10^{-5}$ Pa). The experimental techniques and single crystals are the same as those used in [3] and [4]. The total impurity content (10-100 ppm) is smaller than the departure from stoichiometry (10^{-4} to 10^{-3} at 1 500 °C). The law which describes the steady state creep is written [1, 5] :

$$\dot{\varepsilon}_S = A\sigma^n P_{O_2}^m \exp - \frac{Q}{kT} . \qquad (1)$$

The aim of the work is to determine the stress exponent n, the oxygen pressure exponent m and the creep activation energy Q. For this we made stress, P_{O_2} or temperature changes and compared $\dot{\varepsilon}_S$ values before and after the changes [1]. Care must be taken to ensure that the specimen has reached thermodynamic equilibrium after P_{O_2} or temperature change [5]. Annealing duration before resuming creep is determined in NiO by nickel vacancy diffusivities, i.e. chemical diffusion [6, 7]. If we use the smallest diffusion coefficient $\tilde{D}$ [6], we find that $\sqrt{\tilde{D}t} = 0.2$ cm for annealing duration of 28 hours, 5.6 hours and 1.4 hour at 1 100 °C, 1 300 °C and 1 500 °C respectively (specimen size : $2 \times 2 \times 5$ mm^3). Long enough annealing has been used to ensure that new equilibrium nonstoichiometry has been reached in the whole specimen; shorter duration can be used, because the diffusion is probably accelerated, at low temperature, by the large amount of dislocations due to plastic deformation. Annealing durations between 1 h and 18 h have been used, depending on temperature creep test, with no influence on m and Q values. Very long annealing does not improve the experiment because it leads to large dislocation recovery, followed by a transient, when resuming creep, which decreases the accuracy of the n, m or Q determination [5].

(*) Part of the thesis of J.C.C., to be submitted.

2. **Results.** — Fourteen NiO single crystals have been strained up to $\varepsilon \sim 0.6$ with σ parallel to $\langle 100 \rangle$. Among then, one was doped with ˜300 ppm Cr; n, m and Q values have been extracted from steady state creep by 20 stress changes, 35 temperature changes and 30 oxygen pressure changes. The stress exponent n decreases from 11.5 at 1 150 °C to 8.5 at 1 350 °C and 6.8 (± 1) at 1 500 °C. This shows that, for an accurate description of results, the power creep law should be replaced by an exponential law, in particular at low temperature and high stress [1]. Values for m and Q are shown in figure 1. The accuracy for m values is not better than ± 0.05 and for Q values ± 1 eV. More experiments would be necessary to decrease the scatter of experimental results. However, it can be seen (Fig. 1) that the minimum value for Q is around 5.2 eV [3] with higher values at higher temperature and lower P_{O_2}. The m values decrease from $m \simeq 0$ to $m \simeq -0.1$ (Fig. 1).

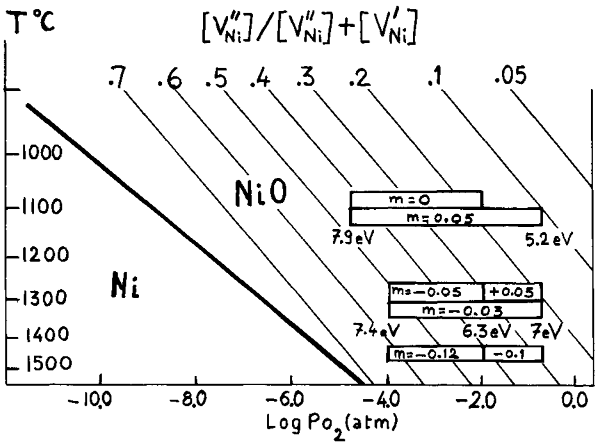

Fig. 1. — Stability range of NiO showing iso-concentration lines for V'_{Ni} and V''_{Ni} as determined by [6]. Activation energies (eV) and P_{O_2} exponent m for creep are shown for T and P_{O_2} creep conditions; m values are shown in rectangles showing the P_{O_2} change used for their determination.

3. **Discussion.** — Nonstoichiometry has been explained in NiO by the presence of large amounts of nickel vacancies V'_{Ni} and V''_{Ni} [6]. Singly charged vacancy concentration $[V'_{Ni}]$ is high at low temperature and high P_{O_2} and $[V''_{Ni}]$ is high at high temperature and low P_{O_2} (Fig. 1) [6]. If we accept the likely assumption that steady state creep is controlled by the diffusion of oxygen [1, 2], we can explain the variation of $\dot{\varepsilon}_S$ with P_{O_2} and determine the nature of the point defect X through which oxygen diffusion occurs. Following a procedure previously developed [5], we deduced eq. (1) from:

$$\dot{\varepsilon}_S = B D_O \sigma^n \tag{2}$$

where D_O is the diffusion coefficient for oxygen:

$$D_O = [X] \, D_X \, f_X \tag{3}$$

[X] : concentration of defect allowing oxygen diffusion i.e. either oxygen vacancy V_O or oxygen interstitial O_i

D_X : diffusion coefficient of X

f_X : correlation factor taken constant.

The P_{O_2} exponent m in eq. (1) is the same as that in the equation giving [X]. We can calculate it with the help of the Kröger-Vink formalism [8].

Results of such systematic calculations are summarized in [8], p. 358 for pure and doped binary oxides. For NiO in the intrinsic state, the results for 10 cases are shown in the table I.

Creep experiments give m values that are close to zero or negative. This indicates that oxygen diffuses through vacancies. Moreover, m values tend to be zero when V'_{Ni} is dominant (Fig. 1) and -0.1 when V''_{Ni} is dominant (Fig. 1). This strongly suggests that the point defect in the oxygen sublattice which explain diffusion controlled creep is $V_O^{\cdot\cdot}$. This result is in agreement with that suggested from an entropy analysis of oxygen self-diffusion [4].

The variation of $V_O^{\cdot\cdot}$ concentration with P_{O_2} and T can be calculated when V'_{Ni} or V''_{Ni} are dominant. The formation equation of V'_{Ni} is:

$$\tfrac{1}{2} O_2 \rightleftarrows O_O + V'_{Ni} + h (\Delta G_4) \tag{4}$$

giving for hole h and vacancy concentration:

$$[h] = [V'_{Ni}] = P_{O_2}^{0.25} \exp - \frac{\Delta G_4}{2\,kT}. \tag{5}$$

We can write for the formation equation of $V_O^{\cdot\cdot}$:

$$2\,h + O_O \rightleftarrows V_O^{\cdot\cdot} + \tfrac{1}{2} O_2 (\Delta G_6) \tag{6}$$

giving with the help of eq. (5):

$$[V_O^{\cdot\cdot}] = \exp - \frac{\Delta G_4 + \Delta G_6}{kT}. \tag{7}$$

As shown in the table I, when V'_{Ni} and $V_O^{\cdot\cdot}$ are the dominant defects in Ni and O sublattices, the concentration of $V_O^{\cdot\cdot}$ is independent of oxygen pressure.

Table I. — *P_{O_2} exponent m for the concentration* [X] *of point defect* X *in the oxygen sublattice for various combinations of oxygen and nickel defects* (*after* [4]).

Defects	V'_{Ni} $V_O^{\cdot}$	V'_{Ni} $V_O^{\cdot\cdot}$	V''_{Ni} $V_O^{\cdot}$	V''_{Ni} $V_O^{\cdot\cdot}$	V'_{Ni}-V''_{Ni} V_O^{*}	V'_{Ni} O'_i	V'_{Ni} O''_i	V''_{Ni} O'_i	V''_{Ni} O''_i	V'_{Ni}-V''_{Ni} O_i^{*}
—	—	—	—	—	—	—	—	—	—	—
m	− 0.25	0	− 0.33	− 0.17	− 0.5	− 0.25	0	0.33	0.17	0.5

When V''_{Ni} is dominant we write :

$$\tfrac{1}{2}\,O_2 \rightleftarrows O_O + V''_{Ni} + 2\,h(\Delta G_8) \qquad (8)$$

$$[h] = 2[V''_{Ni}] = 2^{1/3}\, P_{O_2}^{0.17} \exp - \frac{\Delta G_8}{3\,kT}. \qquad (9)$$

Then from reaction (6) and (8) :

$$[V_O^{\cdot\cdot}] = 2^{2/3}\, P_{O_2}^{-0.17} \exp - \frac{\Delta G_6 + (2/3)\,\Delta G_8}{kT}. \qquad (10)$$

A comparison of eqs. (7) and (10) shows that the activation energy for oxygen diffusion controlled creep is different depending on whether V'_{Ni} or V''_{Ni} is the dominant point defect. The difference in diffusion activation energy is : $\frac{2}{3}\,\Delta G_8 - \Delta G_4$.

We can estimate its value from electrical conductivity σ_e measurements [6] :

$$\sigma_e = e\mu[h] \qquad (11)$$

where μ is the hole mobility. When V'_{Ni} is the dominant point defect, the activation enthalpy for σ_e can be deduced from (5) and (11) :

$$\Delta H_\sigma = -\,k\,\frac{\partial \ln \sigma_e}{\partial\, 1/T} = \frac{\Delta G_4}{2} + \Delta Hm \qquad (12)$$

where ΔHm is the activation enthalpy for hole mobility.

Experimental determination gives [6] :

$$\Delta H_\sigma \simeq 0.9\ \text{eV}. \qquad (13)$$

When V''_{Ni} is the dominant point defect one finds from (9) and (11) [6] :

$$\Delta H_\sigma = \frac{\Delta G_8}{3} + \Delta Hm \simeq 1.2\ \text{eV}. \qquad (14)$$

Eqs. (12), (13) and (14) allow an estimate to be made of the maximum variation in diffusion activation enthalpy :

$$\tfrac{2}{3}\,\Delta G_8 - \Delta G_4 \simeq 0.6\ \text{eV}. \qquad (15)$$

When V''_{Ni} is the dominant point defect (high T, low P_{O_2}, Fig. 1), the activation enthalpy for oxygen diffusion exceeds by 0.6 eV that corresponding to V'_{Ni}. A value of 5.6 ± 0.5 eV has been found for oxygen self-diffusion [4]. For creep, values are between 5.2 ± 1 eV and 7.9 ± 1 eV (Fig. 1). In both cases, results are rather inaccurate, but they are in qualitative agreement. In order to have a full understanding of activation process, one must take into account the following facts :

(i) The Arrhenius plot for oxygen self-diffusion in air has been analysed as a straight line [4]. There might be some curvature at high temperature giving larger activation energies as suggested from point defect analysis.

(ii) Q has been determined with the help of eq. (1) which gives large n values. This means that Q is better written as $Q_0 - V\sigma$ [1], where Q_0 must be compared to diffusion data. This would explain values for creep smaller than for diffusion.

(iii) Eq. (2) is based on the assumption that creep is diffusion controlled. Dislocation point defect interaction jog formation and mobility energies might influence the creep rate and give activation enthalpies larger than diffusion enthalpies [1].

Oxygen pressure dependence is then a better way for checking the models.

Such an experiment has been performed on a 300 ppm chromium doped specimen. Calculations can be performed with one of the neutrality equations :

$$[V'_{Ni}] = [Cr^{\cdot}_{Ni}] \qquad (16)$$

or

$$2[V''_{Ni}] = [Cr^{\cdot}_{Ni}]. \qquad (17)$$

For $V_O^{\cdot\cdot}$, m values of 0.5 with eq. (16) and $m = 0$ with eq. (17) can be deduced ([8], p. 359). Creep experiments give a m value of 0.35 (two measurements) between air and $P_{O_2} = 1\,\%$ atm. at 1 120 °C and $m \simeq -0.01$ (two measurements) between $P_{O_2} = 1\,\%$ atm. and 2×10^{-5} atm. at 1 320 °C. If the diagram of the figure 1 is still valid for doped NiO, the creep conditions correspond respectively to dominant V'_{Ni} and V''_{Ni}. Experimental values are in fair agreement with predictions from calculations assuming, again $V_O^{\cdot\cdot}$ as a dominant defect in the oxygen sublattice.

4. **Conclusion.** — In a previous study of this type, high temperature creep of Cu_2O has been explained in terms of oxygen self-diffusion and suggested an interstitial point defect in the oxygen sublattice [5]. This result is in fairly good agreement with more recently performed [9] oxygen diffusion measurements. The situation in NiO is more complicated because non-stoichiometry is described by a mixture of V'_{Ni} and V''_{Ni}. However, creep experiments lead to the conclusion that $V_O^{\cdot\cdot}$ is the dominant point defect in the oxygen sublattice.

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References

[1] Bretheau, T., Castaing, J., Rabier, J. et Veyssière, P., *Adv. Phys.*, to be published.

[2] Mitchell, T. E., Hobbs, L. W., Heuer, A. H., Castaing, J., Cadoz, J., Philibert, J., *Acta Metall.*, to be published.

[3] Cabrera-Cano, J., Dominguez-Rodriguez, A., Marques, R. and Castaing, J., *J. Physique Lett.* **39** (1978) L-451.

[4] Dubois, C., Thèse, Université Paris 11, Orsay.

[5] Bretheau, T., Marhic, C., Spendel, M. and Castaing, J., *Philos. Mag.* **35** (1977) 1473.

[6] Farhi, R. and Petot-Ervas, G., *J. Phys. Chem. Solids* **39** (1978) 1169 and 1175.

[7] Nowotny, J. and Sadowski, A., *J. Am. Ceram. Soc.* **62** (1979) 24.

[8] Monty, C., *Défauts ponctuels dans les solides* (Les Editions de Physique, Orsay, France), Confolant 1977, Ch. XII.

[9] Perinet, F., Barbezat, S., Monty, C., Conf. on Lattice defects in ionic crystals, Canterbury Sept. 1979, *J. Physique*, to be published.