Pure diffusional creep of NiO polycrystals

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Pure diffusional creep of NiO polycrystals

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Résumé. — Des essais de fluage en compression ont été faits sur des polycristaux de NiO, dans l'air et l'argon, à des températures entre 1 100 et 1 500 °C (0,61 à 0,79 T_F) sous des charges correspondant à des contraintes initiales entre 6 et 90 MPa. Le fluage Nabarro a été observé à faible contrainte ; la vitesse de déformation et la diffusivité de l'oxygène montrent une bonne corrélation.

Abstract. — Compressive creep testing of polycrystalline NiO has been performed in air and argon, at temperatures between 1 100 and 1 500 °C (0.61 to 0.79 T_M) under loads corresponding to initial applied stresses from 6 to 90 MPa. Nabarro creep was observed in the lower stress range ; creep rate and oxygen diffusivity show a good correlation.

1. Introduction.

High temperature creep through dislocation motion has been extensively studied for non-stoichiometric $Ni_{1-x}O$ [1]. It was concluded that the controlling mechanism was the climb of dislocations which directly depends on the diffusion of the slowest species [2] i.e. oxygen in NiO [1]. This relation between creep and diffusion data is not direct, as it involves complex elementary processes for the climb of dislocations [1]. The usual straightforward creep equations may be too approximate in the case of compounds [2]. On the contrary, pure diffusional creep involves no dislocations ; it then gives direct information on diffusion of the slowest species. We have performed creep tests on NiO polycrystals in order to observe pure diffusional creep and derive characteristic on point defects in the oxygen sublattice. These characteristics are then compared with the results deduced from single crystal creep involving dislocation motion.

2. Experimental techniques.

2.1 ELABORATION AND CHARACTERIZATION OF POLYCRYSTALS. — High purity NiO powder, provided by Johnson Matthey, was used to make polycrystals. The powder was cold pressed and then heat treated at 1 200 °C in air during 3 days. The density of the resulting sintered materials was 70 % of the theoretical density of 6.8 g/cm^3. Specimen densities were determined from the weight to volume ratio.

In order to obtain low porosity materials, we have submitted the sintered polycrystals to a large deformation ε between 0.8 and 1.5. A compressive stress was applied at temperatures between

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1 150 °C and 1 300 °C during 6 to 24 h, in air. The stresses, calculated as loads divided by initial surfaces, were between 5 and 20 MPa. Specimen densities were found between 92 % and 96 % of the theoretical density; higher applied loads and temperatures gave higher densities.

Mechanical polish followed by chemical etching in H_3PO_4 at 160 °C during 15-20 min. was used to reveal grain-boundaries. Although large strains were achieved, grains are not elongated (Fig. 1), probably because of low deformation stress. The average grain sizes were measured by counting over 500 grains; it was found between 6 and 12 µm, with higher values for high temperature compressions.

Fig. 1. — Microstructure of NiO polycrystals revealed by chemical etching after densification.

2.2 CREEP TESTS. — Creep tests have been performed using a constant load compression machine made of alumina [3], using procedures described in earlier papers [1, 2]. Parallelepipedic specimens with 5 × 3 × 3 mm dimensions were deformed at temperatures between 1 100 °C and 1 500 °C in air (0.21 atm) or in flowing argon with an oxygen partial pressure P_{O_2} of 10^{-5} atm. Stresses from 6 to 90 MPa were applied in the same direction as during the densification compression. Creep data were analysed using the traditional creep law [2] :

$$\dot{\varepsilon} = \sigma^n d^{-\alpha} P_{O_2}^m \exp - \frac{Q}{kT}. \tag{1}$$

d = grain size,
$\dot{\varepsilon}$ = strain rate.
The parameter n, m, α and Q are characteristic of the creep mechanisms.

3. Results and discussion.

A typical creep curve plotted as $\log \dot{\varepsilon} - \varepsilon$ is shown in figure 2. There is not a prominent transient creep as usual for diffusional creep, no substructure being formed before reaching a steady state.
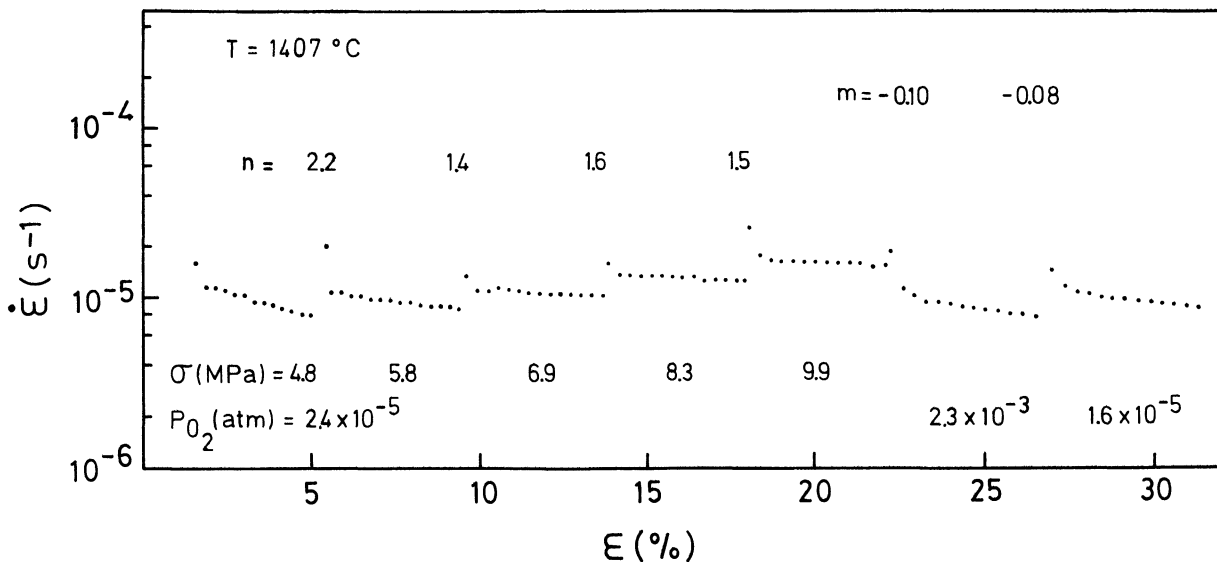
Fig. 2. — Compression creep curve of a NiO polycrystal with 6 % porosity and 8 µm grain size. Stress and P_{O_2} changes have been performed.

Various stress and P_{O_2} changes are shown, which allow to determine the parameters n and m. For a P_{O_2} change, the specimen is unloaded and annealed, before resuming test, in order to reach the new thermodynamic equilibrium i.e. the new values of concentrations for majority point defect (V_{Ni}), as well as for minority point defect.

Stress exponents n are plotted in figure 3. Below $\sigma = 20$ MPa, n is about 1.5 and above $\sigma = 30$ MPa, n increases to reach values of about 7 at 90 MPa. Dislocation creep associated with large n values, has been observed in single crystals for stresses of 25 to 120 MPa [1].
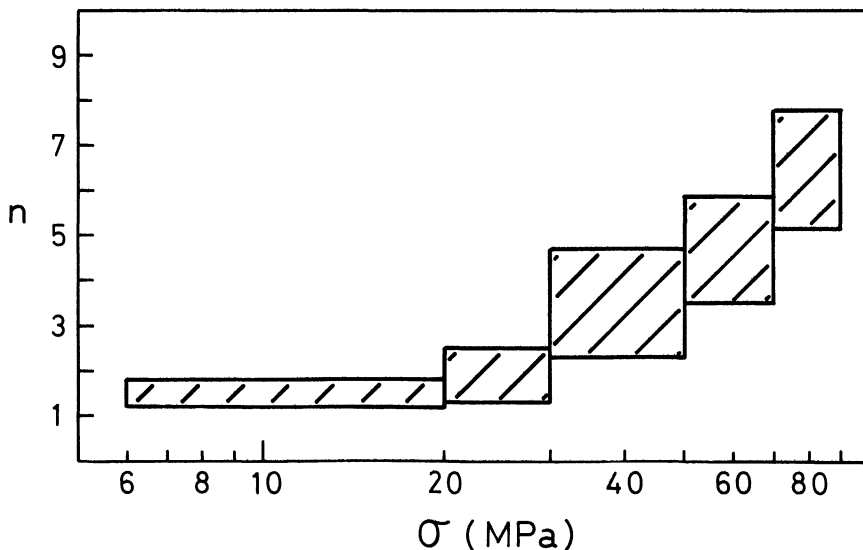

Fig. 3. — Stress exponents n versus applied stresses σ at temperatures between 1 100 ºC and 1 500 ºC in P_{O_2} of 0.21 atm and 10^{-5} atm.

Values of n between 1 and 2 have been already observed in some ceramic oxides [4], SiC [5], Cu_2O [3] and also in NiO which has been studied in 3 point bending using low density poly-crystals [6]. They are attributed to plastic deformation by pure diffusional creep, diffusion in the bulk or in grain-boundaries controlling the strain-rate; grain-boundary sliding is required to accommodate the deformation [7, 8]. Increase in n occurs when other creep mechanisms become predominant. They involve dislocation multiplication, as well as possibly grain boundary slid-ing [7]. The role of diffusion can be easily assessed by studying the influence of P_{O_2} on creep rate.

We have measured the P_{O_2} exponents m for various temperature a stresses below 20 MPa in order to characterize the pure diffusional creep regime. The results are shown in figure 4 together with those obtained previously for single crystals [1]. Very close to zero at low T and high P_{O_2}, m tends to small negative values at high T and low P_{O_2}; these behaviours look very similar for single crystal dislocation creep and polycrystal diffusional creep (Fig. 4). This strongly suggests that the same fundamental process controls the kinetics of creep in both cases, i.e. volume diffu-sion of oxygen via a vacancy $V_O^{\cdot\cdot}$ mechanisms; m changing between zero ($V_O^{\cdot\cdot}$, V_{Ni}') and -0.17 ($V_O^{\cdot\cdot}$, V_{Ni}'') as explained in the paper on single crystals [1]. This conclusion suggests that diffusion takes place in the volume of the grains (Nabarro creep), not in the boundaries (Coble creep). An additional experimental evidence comes from the determination of the parameter α of equa-tion (1). A preliminary determination has been made on polycrystals with grain sizes between 6 and 12 μm; a value of α close to 2 was found, corresponding to Nabarro creep [7, 8].
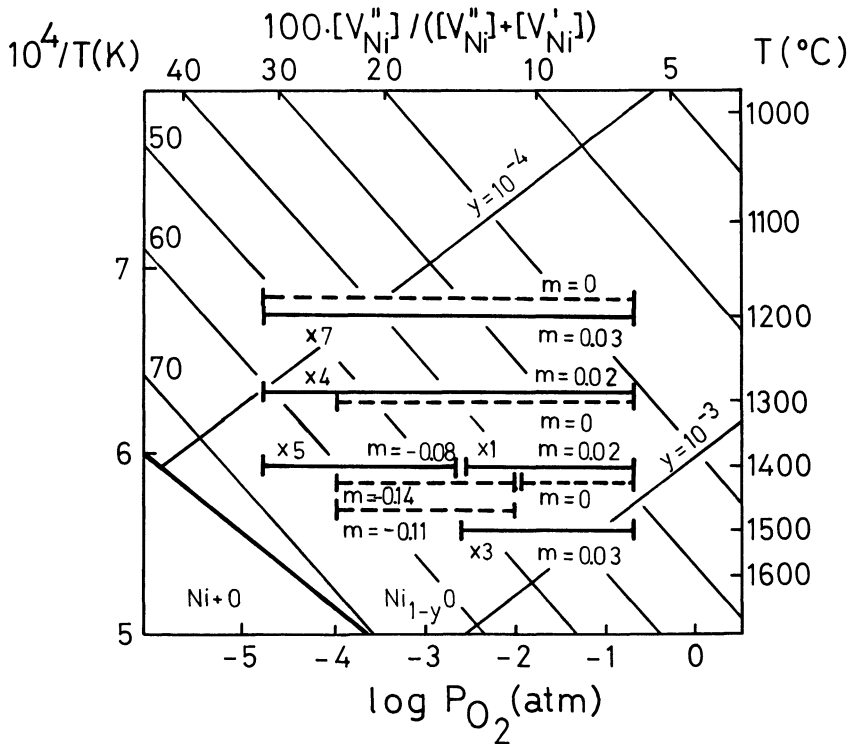

Fig. 4. — Exponents m of P_{O_2} plotted on the $T - P_{O_2}$ equilibrium phase diagram of $Ni_{1-y}O$. Lines show non stoichiometry y and fraction of doubly charged vacancies $[V_{Ni}'']/([V_{Ni}''] + [V_{Ni}'])$. Broken lines indicate P_{O_2} changes and m values for single crystals [1] and full lines are for polycrystals with indications of number of determinations.

Finally, we have determined the constant B of the Nabarro creep equation (7) :

$$\dot{\varepsilon} = B \frac{\Omega \sigma}{kTd^2} D_0 \exp - \frac{Q}{kT},$$

where we take for the volume of NiO, $\Omega = 1.83 \times 10^{-23}$ cm^3, $D_0 = 50$ cm^2/s as obtained by C. Dubois [9] and $Q = 3.8$ eV average value found in these experiments. We have obtained values between 8 and 60, which is a reasonable agreement with theoretical predictions [7, 8].

We have shown that below 20 MPa, polycrystalline NiO with grain size between 6 and 12 μm deforms in compression by a pure diffusional creep at temperatures of 1 100-1 500 °C ; creep rate is directly related to bulk oxygen self-diffusion. More experiments are in progress to study the influence of grain size on a large range of values and to determine accurately activation energies of creep.

Acknowledgments.

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