

High-temperature *in situ* experiments in HVEM on NiO single crystals

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High-temperature *in situ* experiments have been performed in the high-voltage electron microscope (HVEM) on NiO single crystals. These high-temperature experiments necessitate special equipment such as a high-temperature (1200° C) double-tilting holder, a high-temperature (1200° C) straining holder and a low light level and high resolution visualization and recording system. Because of the reduction of the oxide at high temperature, these experiments were not possible when the partial pressure of the oxidizing agents was lower than 10^{-2} Pa (10^{-4} torr), which is in good agreement with the Ni-NiO equilibrium diagram. The evolution of a dislocation dipole has been observed and recorded during these experiments, thereby demonstrating the possibilities of high-temperature *in situ* experimentation on ceramic materials.

1. Introduction

Knowledge of the plastic deformation behaviour of NiO [1, 2] is essential in understanding the role played by the protective oxide scales formed during the oxidation of nickel and its alloys. Although several macroscopic constant strain rate or creep tests have already been carried out on NiO, transmission electron microscope (TEM) observations are necessary to identify the rate-controlling deformation processes. Some TEM observations have already been performed on NiO [3, 4], and the dislocation configurations have been found to be similar to those observed in NaCl [5] and MgO [6]. At room temperature, a high density of long edge-dislocation dipoles $\mathbf{b}\langle 110\rangle$ is observed in the $\{110\}$ glide planes. The formation of these dipoles, which are directed along the $\langle 100\rangle$ directions, is due to the presence of immobile jogs on mobile screw dislocations. During deformation these dipoles act as barriers against crossing dislocations. From these interactions results the division of the dislocation dipole into loops [3, 4]. Dislocation dipoles have

also been observed at high temperatures, i.e., $>1000^\circ\text{C}$ [3]. But, due to thermal diffusion the dipole configuration is not stable at high temperature, i.e., the dipoles shrink into loops which in turn disappear. Some preliminary *in situ* deformation and annealing tests are reported in the present paper, thereby confirming the above mechanisms.

2. Experimental techniques

The *in situ* experiments were performed on NiO single crystals obtained by the zone-melting technique in an arc image furnace. A spectroscopic analysis of the crystals gave 10 ppm of Mg and 15 ppm of Si as impurities. The specimens were obtained through mechanical sawing and polishing. Annealing tests were performed on small discs 3 mm in diameter and 0.5 mm in thickness, whereas small slabs (3 mm \times 8 mm \times 0.5 mm) were used for the *in situ* deformation tests. The shape and crystallographic orientation of the tensile specimens were identical to that used by Appel *et al.* [5] (Fig. 1). These tensile specimens were

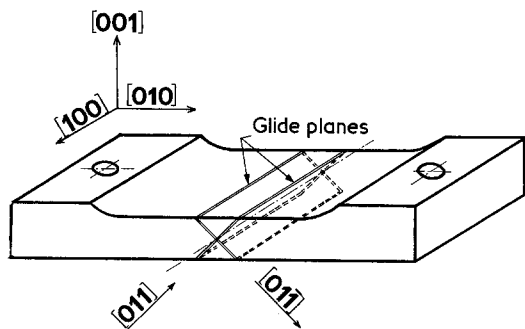


Figure 1 Schematic diagram indicating the glide planes in the tensile specimen used for the *in situ* tensile tests in HVEM.

neither glued nor clamped on the jaws, but mechanically fixed by means of two small screws. The crystallographic orientation of the specimen plane was the same in both cases, i.e., tensile specimens and annealing specimens. Final thinning was obtained through chemical polishing. The solution used in this jet-polishing technique consisted of one part of nitric acid and three parts of phosphoric acid. Polishing was performed at a temperature of 140°C (Fig. 2). As compared to the ion-beam thinning technique, the polishing time is much shorter (30 min instead of 1 or 2 days). Moreover, this chemical process also has the advantage of avoiding radiation damage.

The high-temperature *in situ* experiments were all performed in a high-voltage electron microscope (1.2 MV). A high-temperature (1200°C) specimen holder designed in Grenoble [8] was used for the *in situ* tensile strain tests, whereas a double-tilting

heating holder (1200°C) designed at ONERA [9] was used for the annealing tests.

To avoid surface effects, the observations must be performed on relatively thick specimens, i.e., thicknesses of 1 or 2 μm. Consequently, these *in situ* experiments not only require a high-voltage electron microscope but also a high-resolution visualization and recording system in order to observe thick specimens without any loss of resolution. Such a high-resolution visualization system has been designed by optimizing the transfer function of each element of the system, i.e., the low light-level TV camera tube, the objective lens and the new transmission phosphor screen [10]. The TV images are recorded with a IVC video recorder. The TV images are then transferred onto a ciné film. However, the TV picture (625 lines at 25 frames sec⁻¹) consists of two scan fields of 20 msec each, whereas the exposure time of a ciné camera filming at 25 frames sec⁻¹ is only 20 msec with a 180° shutter. With the simpler method, called suppressed field recording, each picture will consist of only half the total number of lines. In the present case, the partial suppressed field method is used. The Cameflex Eclair ciné camera runs at 16 $\frac{2}{3}$ frames sec⁻¹ and uses a 240° shutter opening so that each shutter opening records two successive fields. Each ciné picture thus has the same resolution as the TV image, and may be enlarged to give information on the evolution of a given process (Fig. 3).

High-temperature *in situ* experiments often has a duration, *t*, of several minutes or even

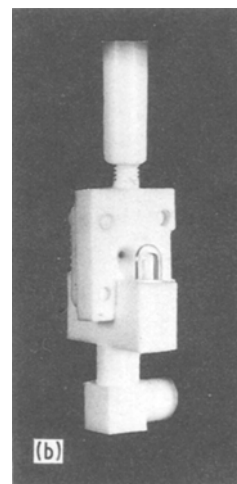
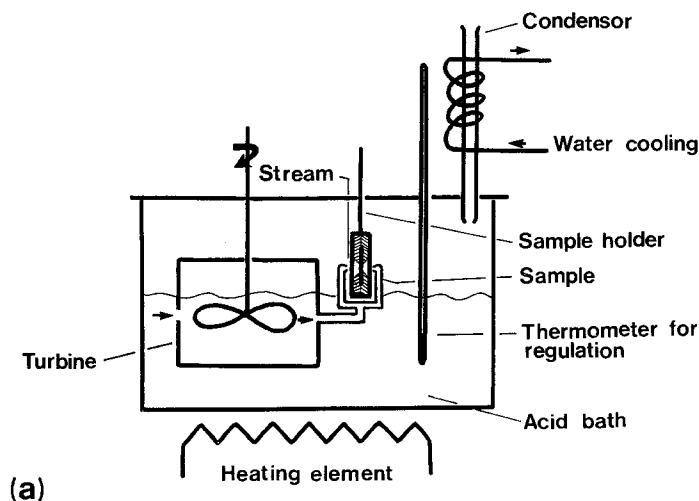


Figure 2 The apparatus used for the chemical polishing of the ceramic specimens. Note that the jet polishing of the specimen is performed above the liquid level. (a) Schematic diagram. (b) Specimen holder.

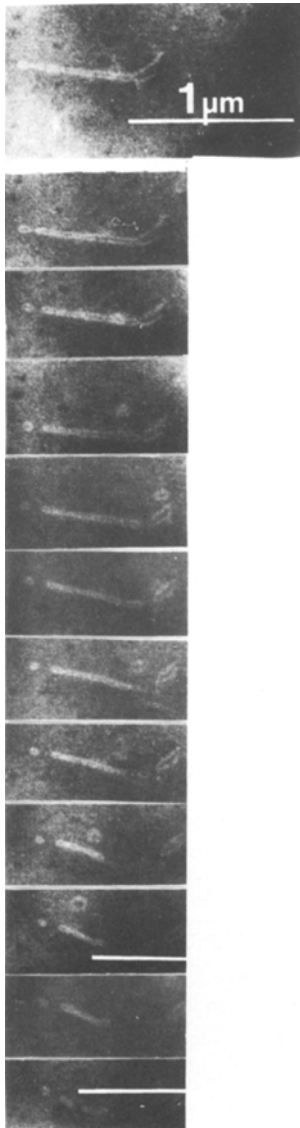


Figure 3 A 15 min sequence showing the evolution of a dislocation dipole in NiO observed directly in the microscope at 1100° C.

several hours. In the case of metals, these experiments necessitate a high vacuum to prevent the formation of a metal oxygen solid solution. The highest admissible pressure of oxidizing agents (oxygen and water vapour) have been determined through the investigation of the oxidation process at low pressure and high temperature. The required pressure (7×10^{-6} Pa = 5×10^{-8} torr) is attained in the high-vacuum specimen chamber designed at ONERA [11]. However, in the case of some oxides, the reduction of the specimen may be observed under such conditions. In the present

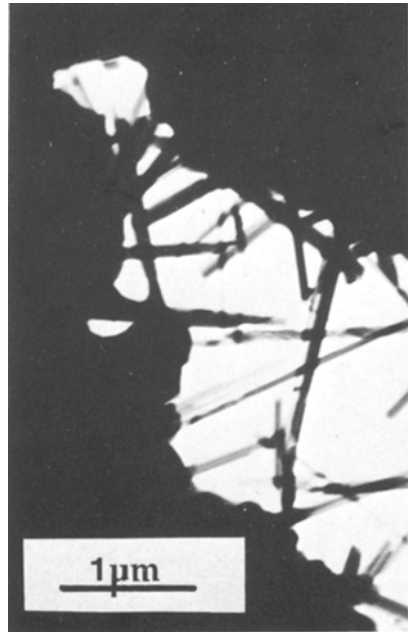


Figure 4 The NiO specimen after heating at 1100° C in the microscope vacuum [10^{-4} Pa (10^{-6} torr)]. The formation of Ni needles may be attributed to the reduction of the oxide.

investigation, the formation of needles was observed in the microscope at a temperature of 1100° C and a pressure of 10^{-4} Pa (10^{-6} torr) (Fig. 4). The microanalysis in a JEOL 200 CX TEM has demonstrated that these needles were in fact nickel. Their formation may thus be attributed to the reduction of the oxide. These observations are in good agreement with the already published Ni–NiO equilibrium diagram (Fig. 5) [1]. According to this diagram, the reduction of the oxide would be observed at a temperature of 1100° C, provided that the oxygen partial pressure was

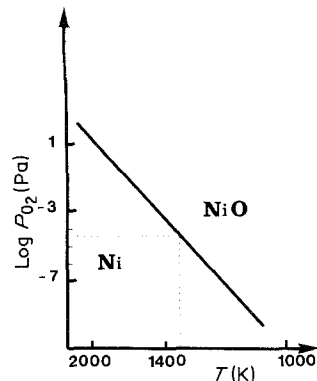


Figure 5 The Ni–NiO equilibrium diagram.

lower than 10^{-3} Pa (10^{-5} torr). However, the reduction of the oxide was not observed during the high-temperature (1100°C) strain experiments performed in Grenoble. This may be attributed to the presence of a gold thermal shield which drastically limits the pumping speed at the specimen level. Due to the outgassing of the ceramic jaws of the straining device, the vacuum level may be supposed to be approximately 10^{-2} Pa (10^{-4} torr). According to the equilibrium diagram, the oxide is stable under such temperature and pressure conditions.

3. Results and discussion

Room-temperature strain experiments have been performed at ONERA [12] and dislocation movements have been observed in NiO specimens. High-temperature (1100°C) strain experiments were performed in Grenoble, but in this latter case, the applied strength was not high enough to deform the NiO specimens. However, the evolution of a dislocation dipole over a time, t , was observed and recorded during these high-temperature *in situ* experiments (Fig. 3). First, the formation of a dislocation loop was observed in the left-hand part of the dipole. Then, due to the shrinking of the dislocation dipole at the other end, an elongated dislocation loop was formed. After a certain time, the elongated loop decreases in length and produces several small loops which in turn disappear by diffusion. However, this evolution of a dislocation dipole into loops has not been observed at temperatures lower than 1100°C . These observations are in good agreement with the previously mentioned mechanisms explaining the formation of dislocation loops from dislocation dipoles in ceramics. At room temperature, the formation of dislocation loops may be attributed to the interaction of the dipoles with mobile dislocations [4]. But at high temperature, the role of diffusion becomes essential and may thus explain the formation of loops from the dislocation dipoles.

4. Conclusions

In conclusion, the present investigation has shown that it is possible to deform NiO single crystals in the microscope at room temperature, since dislocation movements have been observed and

recorded. High-temperature *in situ* deformation tests may also be performed on NiO provided that the conditions of stability of the oxide are fulfilled. The sequence showing the evolution of a dislocation dipole at 1100°C (Fig. 3) clearly demonstrates the possibilities of the high-temperature *in situ* experimentation on ceramic materials.

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