Microhardness of aged NiO single crystal

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Microhardness of aged NiO single crystal

J. Cabrera-Cano, A. Dominguez-Rodriguez, R. Marquez and J. Castaing (*)

Departamento de Optica de la Facultad de Ciencias de la Universidad de Sevilla, Spain

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Résumé. — On a étudié l'effet du vieillissement sur les propriétés plastiques de monocristaux de NiO dopés avec 20 à 2 500 ppM de manganèse à l'aide de mesures de microdureté et de longueur de bande de glissement. Un maximum de microdureté apparaît après des temps très courts de vieillissement à 550 °C et 850 °C ; par contre, les longueurs de bande de glissement ne passent pas par un minimum et indiquent un durcissement seulement à 550 °C. Ces résultats peuvent être attribués à divers états d'agrégation des défauts ponctuels.

Abstract. — The effects of ageing on the plastic properties of NiO single crystals were determined in samples doped with 20 ppM to 2 500 ppM manganese. Microhardness and slip band length were measured. Maximum microhardness occurs for very short ageing time at 550 °C and 850 °C ; on the contrary, slip band length shows no minimum and shows strengthening only after ageing at 550 °C. These effects can be attributed to various aggregation states of point defects.

1. **Introduction.** — Dislocation mobility is very sensitive to atomic arrangement ; short and long range order of point defects, pre-precipitation and precipitation have a great influence on dislocation mobility and then on mechanical properties. The microhardness test has been much used to study the plastic deformation material undergoing structural change [1] ; we have used it to study the behaviour of manganese doped nickel oxide single crystal. In a previous study [2], it was shown that nickel oxide single crystal containing Mn^{+++} is strengthened at about 500-600 °C. This investigation reveals that pre-precipitation or point defect ordering influences the mechanical properties after annealing at 550 °C in air, but not after 850 °C annealing.

2. **Experimental procedure.** — 2.1 SAMPLE PREPARATION. — The NiO single crystals were obtained by the melt zone method, using an image furnace [2]. Different amounts of MnO_2 were mixed with high purity NiO powder in order to obtain different impurity concentrations. Atomic absorption spectroscopy was used to determine the dopant levels in the final crystals. The concentrations are respectively 5 000-2 500, 1 000-350, and 100-20 ppM before and after melting, showing manganese loss during crystal growth.

(*) Permanent address : Laboratoire de Physique des Matériaux, C.N.R.S. Bellevue, 92190 Meudon (France).

Slabs parallel to { 100 }, about 2 mm thick, were cleaved from these crystals. These slabs were mechanically polished with diamond powder of 8, 5 and 2 microns and, afterwards, chemically polished by immersion for an hour in an agitated 85 % H_3PO_4 bath heated to 160 °C.

After the surface preparation, the samples underwent a thermal treatment consisting of annealing in air for 50 hours at 1 200 °C followed by rapid quenching to room temperature. The annealing time is believed long enough to reach thermodynamic equilibrium. Moreover, from the phase diagram and present work, this treatment ensures that Mn impurities are mostly in the form of Mn^{+++} ions [2]. No loss manganese is expected during the annealing. The ageing of the samples has been carried out in air at two temperature i.e. 550 °C and 850 °C. The samples were introduced into the furnace on a light platinum crucible which allowed them to reach the desired temperature quickly.

2.2 MECHANICAL TEST. — Microhardness testing was carried out at room temperature with a conventional Zeiss Vickers indenter. A 50 gram load was used throughout the study, because this was enough to avoid any anomalous creep phenomena when the time of full load applications was 30 s. Cracks were very seldom observed. Care was taken to put the diagonal of the indenter parallel to ⟨ 100 ⟩ directions. Measurements for various ageing times were performed either on the same sample or on different samples ;

no differences were observed between these two cases.

Slipband lengths were measured after etching in an appropriate corrosive bath ; the etching of our specimen was difficult because of impurity effects. Samples with different Mn concentrations behave in different ways. We have tried various etching baths based on mixtures of H_3PO_4 and HNO_3 at temperatures from 110 °C to 130 °C. The configuration of dislocations around an indentation shows long bands (⟨ 110 ⟩ directions) which correspond to emerging edge dislocations, while shorter bands (⟨ 100 ⟩ directions) correspond to screw dislocations for a { 110 } ⟨ $\bar{1}$10 ⟩ glide system [1].

3. **Results.** — 3.1 MICROHARDNESS. — The microhardness-ageing time profiles obtained have been plotted in figures 1 and 2. Each one of the points plotted represents the average value obtained from at least five microhardness measurements. The bars show the dispersion of these values.

The principal feature of all the curves is the appearance of a maximum at very early ageing times. These maximum values do not vary with the impurity concentration in a significant way. The position and the shape of the maximum do not change significantly when the temperature is changed (Figs. 1 and 2). After the maximum, microhardness reaches a constant value.

Experiments were performed to check the influence of surface preparation. The variation of the microhardness measured on a cleaved face is similar to that measured on a polished face (see section 2). An additional experiment was made on a 350 ppM doped NiO crystal in order to study the influence of surface preparation just before the microhardness test. Measurement on a surface freshly cleaved after the 1 200 °C anneal gives a value of 5 970 MN/m^2 ; after 5 min. ageing at 550 °C, a value of 6 345 MN/m^2 is obtained on a surface either freshly cleaved or exposed to air during ageing. These values are about 8 % larger than the corresponding ones of figure 1.

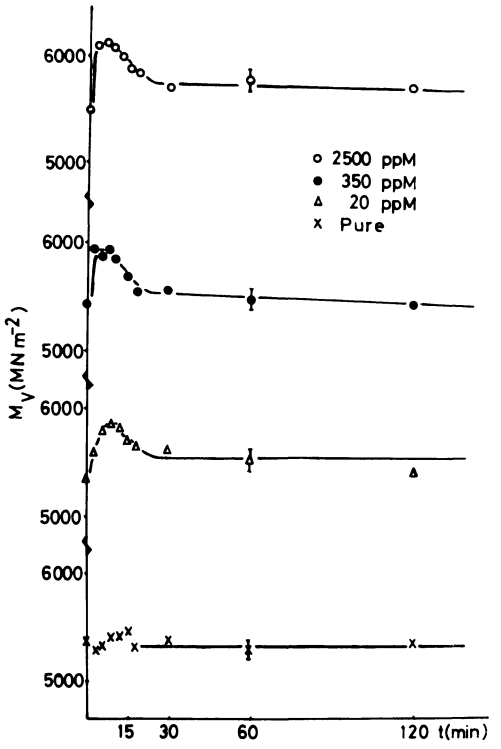

Fig. 1. — Microhardness *vs* ageing time at 550 °C for various Mn concentrations.

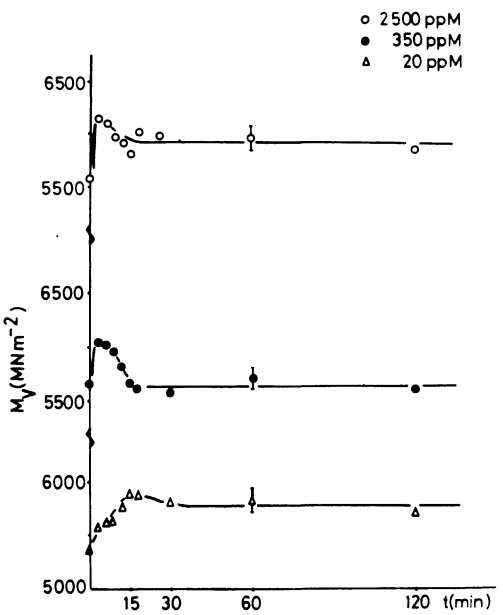

Fig. 2. — As figure 1 after ageing at 850 °C.

3.2 SLIP BANDS. — The dependance of the inverse of slip band length (ISB) with ageing time has been

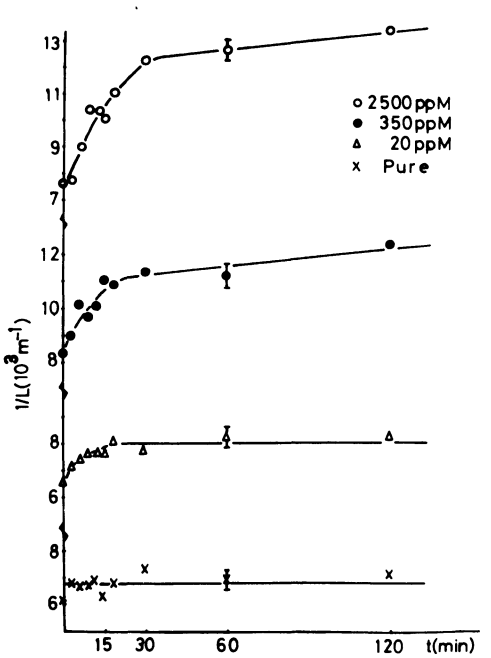

Fig. 3. — Inverse slip band lengths (ISB) *vs* ageing time at 550 °C for various Mn concentrations.

plotted in figures 3 and 4. ISB length is often correlated with flow stress [3, 4, 5]. Ageing at 550 °C leads to a large change in ISB; there is no change in ISB after 850 °C ageing although microhardness behaves similary at the two temperatures.

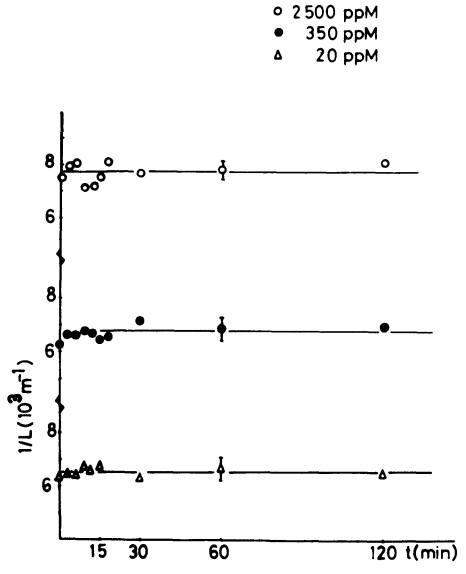

Fig. 4. — As in figure 3 after ageing at 850 °C.

4. **Discussion.** — The combined use of indentation and slip band etching is a convenient and cheap way to study the plastic behaviour of single crystals under various conditions. Many authors used these techniques to study plastic properties of Fe doped MgO; they deduced the critical resolved shear stress (CRSS) from calibration curves relating ISB and CRSS observed by standard bending [3, 4, 6] or compression [7] tests. The results are summarized in table I.

Srinivasan and Stoebe [8] obtained an increase in room temperature compressive CRSS in 40 ppM Fe doped MgO after 1 hour annealing at 700 °C. The strengthening is attributed to $MgFe_2O_4$ precipitates. Several inconsistencies appear among these results (table I); particularly striking are the discrepancy in optimal annealing time between Wicks' [6] and others [3, 4, 7], and the similarity in CRSS values for materials which differ by an order of magnitude in doping level.

In fact several mechanisms must be responsible for the strengthening of MgO and NiO. First, point defect clustering or pre-precipitation must occur involving atomic motion on a few atomic distances which takes place in a short time. The clustering has been seen in MgO by electron paramagnetic resonance (E.P.R.) [6] and the mobility of point defects is shown by the Portevin Lechatelier effect observed in NiO above 400 °C [2]. A second process involves nucleation and growth of second phase precipitates through long distance diffusion.

If one mechanism acts, ISB or CRSS should steadily increase with annealing time. At 550 °C, the rapid increase of ISB (Fig. 3) is probably due to defect clustering similar to that observed in MgO (550 °C for NiO and 800 °C for MgO are $0.35\ T_M$); the slower increase of ISB, after 30 min above 350 ppM (Fig. 3), may be attributed to precipitates, although no precipitates were observed by TEM after 4.5 hours annealing [2]. This means that the solubility limit of Mn^{+++} in NiO at 550 °C is below 350 ppM, but that point defect clustering occurs even at such a low concentration level as 20 ppM. At 850 °C no hardening appears, there is neither clustering nor precipitation; the solubility limit is larger than 2 500 ppM (Fig. 4).

Hardness behaviour is more difficult to understand (Figs. 1 and 2). Kruse and Fine [4] mentionned that hardness values in MgO go through a sharp maximum similar to that shown in figures 1 and 2. The shape of their curves (hardness and ISB or CRSS *vs* ageing time) changes neither with impurity concentration nor with temperature (from 550 °C to 800 °C), a result rather inconsistent with a precipitation mechanism.

Dekker and Rieck [10] have observed microhardness variations in manganese aluminate spinels after various annealing times; they conclude that the increase in hardness is due to unobservable pre-precipitation. The hardness value depends on many parameters such as indenter orientation, work hardening rate [1, 10, 11], surface effects [1]... The experiments on cleaved faces of NiO (see section 3-1) seem to preclude any surface effects on the variation of microhardness with ageing time. The short time

Table I. — *Characteristics of* MgO *strengthened by spinel precipitates after* 800 °C *annealing.* CRSS *was measured at room temperature by the means of microhardness and slip band length measurements.*

Reference	Davidge [3]	Kruse [4]	Wicks [6]	Knoch [7]
Fe^{3+} concentration atomic ppM	3 600	1 400 to 36 500	640	5 360
CRSS before annealing (MN/m^2)	130	80 to 250	125	130
Maximum CRSS (MN/m^2)	170	130 to 380	190	180
Annealing time for maximum CRSS	20 min.	15 min.	30 h	20 min.
Maximum annealing time	100 h	1.5 h	500 h	200 h

maximum is observed on strengthened NiO (Fig. 1) and on non-strengthened NiO (Fig. 2) as well as in MgO [4] at any Fe concentration.

It would be very difficult to put forward an interpretation since the origins of the hardness value [12] are much less understood than those of the slip band length [14].

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