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GRAIN BOUNDARY STRUCTURE IN NiO

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Abstract - Transmission electron microscopy is used to study the structure of grain boundaries (GBs) in NiO. <001> tilt GBs in NiO are generally found to be faceted. Structural periodicities within facets have been observed at low and high misorientation. An effective reduced atomic density at the GB within a region of 0.5-0.8 nm in width is suggested by the defocus contrast behavior of high-angle tilt and twist GBs.

1 - INTRODUCTION

The properties of most ceramic materials strongly depend on the grain boundary (GB) structure and properties. Nevertheless, our knowledge of GBs in ceramics is quite limited and few studies exist of the microstructure of high-angle GBs in transition metal oxides. For the most part the present investigation considers tilt GBs in NiO bicrystals with a misorientation axis near <001>. Conventional transmission electron microscopy (TEM) is used to observe the structure of GBs for different boundary planes and misorientation angles \( \theta \). Questions of interest concern the boundary width, boundary faceting and structural periodicities within the facets. The outstanding feature of all our high-angle boundaries observed so far is their defocus contrast behavior, which implies a considerable degree of openness of the GB structure at the boundary.

2 - EXPERIMENTAL

NiO single and bicrystals were grown from high purity (99.999%) NiO powder in an arc image furnace using the Verneuil technique. An atmosphere of \( \text{P}_{\text{CO}_2}/\text{P}_{\text{CO}} = 200 \) was used in order to maintain growth conditions reasonably close to stoichiometry. High angle NiO GBs grown in air often show macroscopic voids at the GB, presumably resulting from the accumulation of nonstoichiometric cation vacancies at the GB when a lower defect concentration is established in the matrix as the sample is cooled. The bicrystals were seeded from two oriented single crystals, that were obtained by cutting a single crystal normal to the (001) planes at \( \pm \theta/2 \) to the (110) planes, where \( \theta \) is the desired misorientation angle. The orientation of this (symmetric) boundary plane between the seeds was generally not maintained in the resulting bicrystals. Macroscopically the intersections of the GB with (001)
planes appeared curved. This feature allowed (in principle) the study of \( <001> \) tilt GBs as a function of the boundary plane for GBs of the same misorientation. The bicrystals were cut close to \((001)_{1,2}\) into slices \(\sim 500 \mu m\) thick. These slices were annealed at temperatures between \(1200^\circ C\) and \(1500^\circ C\), held at \(1100^\circ C\) for several hours in \(CO_2/CO = 100\) before quenching them to room temperature. An ultrasonic cutting tool was used to cut \(3 \mu m\) diameter discs from the annealed slices. The discs were ground to a thickness of \(100-140 \mu m\). By further grinding and polishing, using a dimpler,* it was possible to obtain thicknesses between 10 and \(20 \mu m\) near the center of the disc. Further reduction to electron transparency was done by argon ion milling on a liquid nitrogen cooled stage. Optical observations were performed on a Leitz Metalloplan under polarized light. For the transmission electron microscopy studies a Philips 400, operated at 120 kV was used. Most observations were performed with the electron beam exactly parallel to the GB misorientation axis.

3 - LOW-ANGLE BOUNDARIES

According to the classic dislocation model /1/ low-angle tilt grain boundaries are composed of dislocations that lie parallel to the tilt axis and whose Burgers vector sum is perpendicular to the GB plane. We studied a few low-angle GBs in the present work to be able to make comparisons between low- and high-angle GB structure and in order to establish a connection with previous work in NiO which has been performed on tilt GBs of relatively low misorientation /2-4/. Several GBs at misorientations near \(\theta = 15^\circ\) were investigated. In one GB, two typical segments of which are shown edge-on in Fig. 1, the tilt axis deviated from \(<001>\) by several degrees. In such a case it is possible to image individual dislocations in the boundary by the defocus technique of Rühle and Sass /4/ even as the sample is viewed closely parallel to the bicrystal rotation axis. The edge-on appearance of individual dislocations as Fresnel-fringe-bounded bright and dark dots in under- and overfocus, respectively, is qualitatively the same for all dislocations within the GB. However, some dots appear larger or have stronger contrast than others. This may be ascribed to differences in the size of the Burgers vector, as suggested by Vaudin, Rühle, and Sass /2/. If these differences in the contrast of individual dislocations are considered it can be easily

Fig. 1 - Complex faceting structures in a tilt GB \((\theta = 13.1)\) with tilt axis near \(<62,55>\). The structural units comprising the GB change with GB orientation. The major facets are asymmetric.

* Manufactured by VCR Group, San Francisco, CA.
recognized from Fig. 1 that even within the facet segments different "structural units" are present. As the average GB plane changes, different facet configurations appear. The facet periods can be quite large and complex repeat-units are also observed. At this point some of the structures have been analyzed in terms of the geometrical GB theory /5/. Similar to the faceting as discussed by Vaudin, Rühle, and Sass, structural periodicities in such GBs may be understood in terms of the O-lattice construction. Figure 2a shows a GB segment without facets, but with a periodic dislocation structure with a repeat-unit of 7.7 nm in length. Figure 2b gives the O-lattice construction for this boundary. The basic periodicity as well as the distances between individual dislocations and the dislocation types as implied from the condition that the sum of the Burgers vector component parallel to the dislocation vanishes over one period /I/ are well represented by the geometrical model. It should be noted that quite frequently minor deviations from perfect periodicity are observed.

According to the O-lattice theory /5/, \( <001> \) tilt GBs will exhibit facet planes symmetric to the (110), \( (010) \), or \( (100) \) planes. The faceting geometry is generally derived by following a path through a maximum number of O-lattice points while staying as close as possible to the average GB plane. In Fig. 3 a GB \( (\theta = 15^\circ) \) whose tilt axis shows a small deviation \( (~2^\circ) \) from \( <001> \) is shown. Here the major facets are indeed symmetric [to \( (100) \) in this case with the dislocation spacing following the relation \( \ell = b/[2 \sin(\theta/2)] \) with a Burgers vector \( b = a<100> \). However, the boundary clearly does not stay close to the average GB plane. Instead, quite long \( (~150 \text{ nm}) \) almost planar facets are joined by short segments in which the GB plane is rotated by \( ~18^\circ \). These secondary facets are asymmetric. They could, in the geometrical model, be formed by a finely stepped arrangement of dislocations in repeat units of three dislocations consisting of one with \( b = a<100> \) and two dislocations with \( b = a/2 <110> \). Clearly, the geometrical model cannot predict the formation of the long facets. In fact, if one drops the assumption that the regular spacing and smallest facet length consistent with the O-net is the energetically favored GB, one has nearly unlimited possibilities for arranging facet length and step height in any given GB. The fact that the large steps with their effective asymmetric GB plane are observed in Fig. 3 must mean that such an arrangement is of lower energy than a uniform distribution of steps and facets. The long facets in Fig. 3a are not perfectly planar but show some secondary faceting as suggested by he slightly displaced double streaks
Fig. 3 - $\theta = 15^\circ$ tilt GB with misorientation axis near $\langle 001 \rangle$. (a) Major facet planes are symmetric relative to $(100)_{1,2}$ and are separated by large steps (~9 nm). The step height (b) is drastically reduced (c) as the average GB plane rotates towards the symmetric orientation. Double streaks in c indicate secondary fine scale faceting in (a), (b).

in the diffraction pattern. Figure 3c shows a short segment of the same GB in a different part of the crystal. A rotation of the average GB plane by $4^\circ$ has been accomplished by a reduction of the height of the large steps in Figs. 3a and b.

4 - HIGH-ANGLE BOUNDARIES

Read and Shockley suggested that the classic model of low-angle tilt grain boundaries can formally be extended to high-angle grain boundaries [1]. The uniform dislocation spacing possible for special misorientations will generally be modulated for arbitrary misorientation angles and can give rise to structural

<table>
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<th>$\Delta F$ (nm)</th>
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<tr>
<td>-200</td>
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<td>-100</td>
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<tr>
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<td>+100</td>
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<td>+200</td>
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Fig. 4 - Through-focus series of high angle ($\theta = 41^\circ$) $\langle 001 \rangle$ tilt GB. $\Delta F = 0$ corresponds to the minimum contrast condition.
units along the GB whose period depends on the deviation from special orientations. The amount of relaxation or the degree to which open spaces exist at the GB of ceramic materials is of particular interest. Recent computer calculations on twist as well as tilt boundaries in NiO have indicated that a considerable effective volume expansion is present in the immediate vicinity of the GB /6-8/.

Electron diffraction studies on twist GBs in NiO /3/ also indicate a considerable increase in interplanar spacing at the GB.

The outstanding feature observed by us so far on all high-angle GB in NiO (\(\theta > 20^\circ\)) is illustrated in Fig. 4. The through-focus series of a \(\theta = 41^\circ \langle 001\rangle\) tilt GB, taken under kinematical conditions, shows a bright band in under-focus and a dark band in over-focus. Similar to the observations of Rühle and Sass on individual dislocations /4/, this behavior indicates a reduced mean inner potential within a band 0.5 to 0.8 nm wide at the GB. This is commensurate with the region of effective reduced density found in lattice statics calculations /6-8/.

It should be noted that this through-focus behavior is typical not only for high-angle tilt GB but also for high-angle twist GBs. Similar defocus effects, although generally over a considerably greater width are often observed in ceramics when an amorphous GB phase is present /9/. In the present case an amorphous GB phase can be excluded on account of the dark-field imaging behavior of the GB, recent lattice fringe observations, and the observed presence of structural periodicities in the GB that will be discussed below. Nevertheless, the influence of possible impurity and charge effects at the GB will have to be taken into account in a quantitative evaluation of the defocus contrast behavior. The above observations in NiO are in contrast to studies of GBs in metals for which a comparable effect in the defocus behavior has not been reported /10,11/.

A qualitative difference between high-angle GB structure in metals and ionic solids seems to be the greater openness of the structure in ceramic oxides which apparently can be maintained by virtue of the strong ionic interactions /6-8/.

While in low-angle GBs individual dislocations are easily resolved by conventional TEM, it becomes quite difficult to discern the primary dislocation period when the tilt angle exceeds \(\sim 20^\circ\). Periodicities corresponding to the expected dislocation spacing based on an extension of the low angle model have, however, been observed down to a period of 0.5 nm and at misorientations up to 35°. While a description of the GB in terms of dislocations may formally be possible at high misorientation, the close proximity or even overlapping at dislocation cores should make such a picture not too useful, although some of the rudimentary geometrical aspects may in fact be retained as evidenced by the observed periodicities. It should be noted that despite the fact that fine-scale periodicities corresponding to the expected primary dislocation spacings have been observed at several high angle GBs, these periodicities are generally not seen at \(\theta > 25^\circ\).

In a general edge-on orientation and under kinematical conditions, most high-angle GBs appear relatively structureless in the direction of the GB plane (see Fig. 4). However, in orientations close to the tilt axis and for favorable imaging conditions most high-angle \(\langle 001\rangle\) tilt GBs show structural periodicities. The latter change with GB plane orientation and take the form of facets and periodicities within the facets. The step height is generally quite small compared to low-angle boundaries. Most high-angle GB facets are asymmetric, i.e., different crystallographic planes are joined at the GB. Such a boundary is shown in Fig. 5. The facets are quite long (\(\sim 22\) nm) and the step height is \(\sim 0.8\) nm. The reciprocal distance between the closely spaced double streaks in the diffraction pattern agree well with the observed length of the facets. The barely visible streaks near (200), suggest the presence of additional structural modulation in the GB with periods of 1.1 and 1.3 nm. These structural periodicities along the facets could, in this case, also been imaged by strain-contrast (see Fig. 5b).

Electron diffraction may be the preferred method for establishing the presence of such structural periodicities. HREM, however, will be necessary to obtain insight into the atomic arrangement.
Fig. 5 - High angle <001> tilt GB (θ = 41°). Asymmetric facet planes are indicated. Barely visible structural detail along facets in (a) is clearly resolved in (b). The structural periodicities concerning facets as well as periodicities within the facets can be obtained from electron diffraction.

Obviously the appearance of facets in high-angle <001> tilt GBs indicates that some GB planes are preferred. The tendency for high-angle <001> tilt GBs to form asymmetric facets suggests that symmetric GB plane orientations do not possess particularly low energies. This is in contrast to what is implied by the geometrical model. Therefore, the 0-lattice construction may not be applicable to high-angle <001> tilt GBs in NiO. On the other hand, the observed periodicities along the facets strongly suggest that the atomic matching between opposing planes must play an important role. A structural unit model may provide insight into the formation of complex structural periodicities along the boundary. Further progress in the understanding of such GBs is expected to come from HREM investigations in conjunction with lattice statics calculations.

REFERENCES