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STRUCTURE AND ENERGY OF Ni/NiO INTERFACES

H.T. Sawhill and L.W. Hobbs

Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

Resume - La structure et l'énergie d'interfaces Ni/NiO développées par oxydation de nickel de haute pureté ont été étudiées par microscopie électronique en transmission. La préparation des échantillons de MET a été effectuée à l'aide d'une méthode permettant d'obtenir des sections parallèles ou perpendiculaires à l'interface. Les structures interfaciales sont discutées à l'aide de modèles de mailles en proche coincidence (type CSL-DSC) ou de coincidence des directions les plus denses. Des franges de moiré ont été observées dans le cas des interfaces correspondant aux relations topotactiques Ni/NiO les plus fortes; un modèle a été développé pour décrire le comportement de ces franges de moiré dans le cas d'une interface inclinée. L'énergie des interfaces Ni/NiO a été estimée à partir des angles diédraux mesurés aux jonctions triples entre les grains de Ni et NiO; les résultats sont exprimés par le rapport entre l'énergie interfaciale Ni/NiO et l'énergie des joints de grains de Ni ou de NiO pour lesquels des estimations suffisamment précises sont disponibles.

Abstract - The structure and energy of Ni/NiO interfaces in oxidized high purity nickel were investigated using Transmission Electron Microscopy. Parallel and transverse section techniques were employed in producing TEM specimens. The Ni/NiO interface structures observed were compared with cell matching models (extended CSL-DSC) as well as models based on matching close-packed directions across the interface. Moiré fringes were observed in interfaces possessing strong topotactic relations between the Ni and NiO. Special attention was paid to the geometry of the moiré fringes and analytic models were developed to describe moiré fringe behavior in inclined interfaces. Estimates for the energy of Ni/NiO interfaces were obtained from dihedral angle measurements at triple grain junctions between Ni and NiO grains. The energies are reported as ratios of Ni/NiO interface energies to either Ni or NiO grain boundary energies for which reasonably precise estimates are available.

Introduction

Metal-metal oxide interfaces constitute a current area of interest in interfacial science and their properties are of considerable technological importance to the oxidation and corrosion science communities. Nickel oxidation provides a convenient method for studying such a heterophase interface because of the inherent crystallographic simplicity (both NiO and Ni have FCC lattice type), and the overall properties of both nickel and nickel oxide have been reasonably thoroughly characterized. In this study, both structure and energy of Ni/NiO interfaces are investigated using transmission electron microscopy. The structures are analyzed in terms of current heterophase interface models while the Ni/NiO interfacial energies are reported as ratios with grain boundary energies of either nickel or nickel oxide. Moiré fringes are reported for certain Ni/NiO interfaces; their image interpretation was investigated through supplemental moiré experiments on gold foils, using Wigner-Seitz cell wall constructions in the analysis.

Experimental Procedure

The details of sample preparation, oxidation and thinning procedures for the high purity nickel (99.995%) are described in detail in reference 1. All samples in this paper were oxidized 15 min. in 3kPa. flowing O_2 at 1273K. Gold twist boundaries were produced by evaporation and welding of gold foils as outlined in reference 2. All boundary and dihedral angle measurements were determined by projection following tilting about two independent axes, checking for consistency using vector algebra for tilted crystals.^[3] The accuracy of projective analysis is limited by the determination of crystal thickness times an inclination factor, and is of the order of 5%.

Ni/NiO Interface Structures

The crystallographic orientation between the NiO grain overlying the Ni grain shown in Fig. 1a is $<3^\circ$ offset from the commonly observed Ni/NiO topotaxy of (001) $[1\bar{1}0]_{Ni} \parallel (111)[1\bar{1}0]_{NiO}$.^[4] The Ni/NiO interface, however, is inclined and possesses quite a different geometry. The interface supports a periodic set of interface dislocations. It was not possible to determine unambiguously the Burgers vectors of these line defects via g·b criterion because of microscope tilting constraints. However, the structures were not visible for g perpendicular to the projected line sense indicating that they are predominantly screw-type. It is presumed that the periodic dislocations accommodate the misorientation from a low energy configuration. The criteria for low energy boundaries in Ni/NiO are not well established, but it appears that parallelism of close packed directions across the interface is important. Fecht and Gleiter (this Journal) demonstrated that low energy configurations between noble metals and ionic crystals are established when there is parallelism of low index planes and close-packed directions across the interface. In this particular topotaxy, there is, in addition to parallel low index planes and close-packed directions, a complementary set of parallel planes at an angle to the interface shown in Fig. 1b. It is possible that the periodic relaxations observed in Fig. 1a result in an effort to accommodate misfit from exact plane matching for boundary orientations largely inclined from the boundary normal illustrated in Fig. 1b.

A second Ni/NiO interface is shown in Fig. 2. In area (A) the geometry is best described by a cell matching near coincidence model $(110)[002][\bar{2}20]_{Ni} \parallel (110)[113]_{\frac{1}{2}}[332]_{NiO}$. The interface normal in area (B) is changing orientation and a concurrent change in interfacial structure is observed. Analysis of this interface is complicated by this non-planar-geometry and final reports will follow further investigation. Although near coincidence atomic site models appear to be appropriate in this case as well as cases presented later in which strong topotaxy across the interface occurs, these models work less well in the case of Fig. 1 in which alignment of low index planes appears to be important.

Moiré Fringes

In order to better interpret information contained in moiré patterns, supplementary experiments were performed using low angle (001) twist boundaries in gold. For

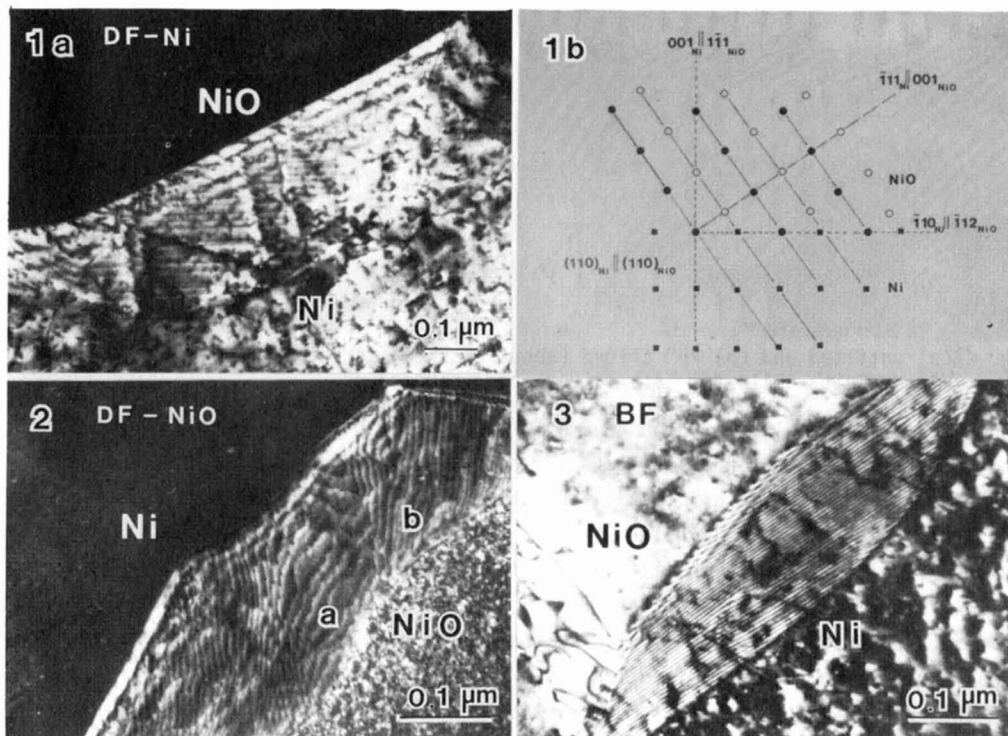


Fig. 1-(a) Ni/NiO interface screw dislocations in inclined interface;
(b) Geometry of Ni/NiO topotaxy shown in Fig. 1a.

Fig. 2-Ni/NiO interface structure changing with boundary orientation.

Fig. 3-Moiré fringes between Ni and NiO in transverse section.

overlapping crystals with small misorientation (twist in this case) imaged under strong 2 beam diffraction conditions, the intensity of the moiré pattern takes the form of eq. [1]:

$$I = F + G \cos (2\pi g \cdot R - x_0) \quad [1]$$

where F , G and x_0 are constants (different for bright and dark field) g is the reciprocal lattice vector of the top crystal (#1) (strong 2-beam condition) and vector R describes the displacement (in this case a rotation) of crystal 2 lattice positions relative to crystal 1 lattice positions in the interface. The resulting intensity is described by a set of cosine fringes, with bright fringes corresponding to the loci of points for which $\cos (2\pi g \cdot R) = 1$ (with $x_0 = 0$). This condition is satisfied whenever R is a lattice vector of crystal 1. Solutions are position vectors in the coordinate frame of lattice 2 with associated displacement vectors equal to crystal 1 lattice vectors. These loci are given by eq. 2:

$y = (I - A^{-1})^{-1}a$ [2] where y are the position vectors in the coordinate frame of lattice 2, A is the crystal misorientation matrix, I is the identity matrix, and "a" are the lattice vectors of crystal 1. When a set of basis vectors of crystal lattice 1 are substituted into eq. 2, a set of basis vectors is produced which form a linearly related lattice, which is equivalently Bollmann's "0" lattice. [5]

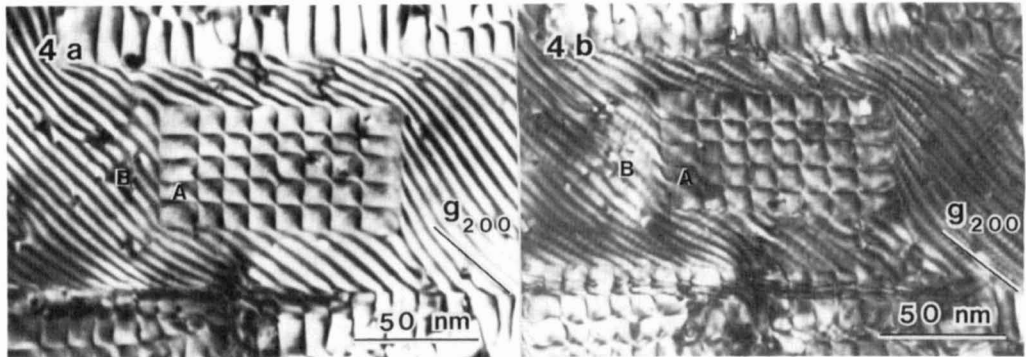


Fig. 4-(a) untilted and (b) 25° tilted (about g) show projective geometry of Wigner-Seitz cells for both moirés and dislocations.

Since Wigner-Seitz cell walls constructed around "0" points correspond to lines of constant displacement of a basis vector of crystal 1, the lines imaged in moiré patterns are cell walls with associated displacement vectors parallel to g . To illustrate this principle, a gold twist boundary was tilted about the (200) axis (axis parallel to g). The untilted and tilted micrographs are shown in Fig. 4a and b. The interface screw dislocations (A) $b = \frac{1}{2}[110]$ and the moiré fringes (B) have geometries described by projections of Wigner-Seitz cell walls onto the plane having normal parallel to the beam direction.

This Wigner-Seitz cell wall construction was also utilized in analysing singularities in moiré patterns for which the reader is referred to reference 6 for details. Since the moiré patterns reflect the displacements across the interface between two overlapping crystals, their presence suggests an absence of dislocation lines with prominent Burgers vectors parallel to g . In Fig. 3 moirés only are observed with no hint of interface structures. From a series of micrographs similar to Fig. 3 we make the generalization that Ni/NiO interfaces with strong topotactic relations across the interface do not appear to contain interface structures with appreciable Burgers vector content. The multibeam interference patterns obtained for epitaxial Ni nickel produced by partial reduction of NiO^[7] show no appreciable deviations from patterns calculated by the present authors in which interfacial dislocations were excluded.

Energy of Ni/NiO Interfaces

The relative energies of Ni/NiO interfaces in oxidized nickel samples were determined from dihedral angle measurements at triple grain junctions in which one or two of the grains were nickel oxide and the remaining grain(s) were nickel. Two examples are presented, the first involves a nickel grain boundary intersecting two Ni/NiO interfaces shown in Fig. 5. The misorientation between the two nickel grains is approximately a 32° rotation about [001] axis, which indicates that its interfacial energy is in the range of a high angle grain boundary in Ni. The two Ni/NiO boundaries exhibit positive curvature as they approach the line of intersection. The relative interfacial energies of the three interfaces is given by the Herring

equilibrium formula which includes interfacial torque terms.[8] Torque terms arise from variations of interfacial energy with surface orientation and are equivalent to the angular derivatives of energy measured on the Wulff plot. Little is known about the geometry of the Wulff plots for Ni/NiO interfaces at the present due to the lack of interfacial energy measurements. The symmetry of the Wulff plot was calculated for several common topotaxies observed in the Ni/NiO system but the results prove to be of little help because of the low symmetries which result. In the present case the symmetry is 1 with symmetries of other cases investigated being typically quite low (e.g. 2 is the symmetry of the Wulff plot for $(111)[\bar{1}\bar{1}0]_{Ni} \parallel (001)[\bar{1}\bar{1}0]_{NiO}$ and $(001)[\bar{1}\bar{1}0]_{Ni} \parallel (112)[\bar{1}\bar{1}0]_{NiO}$). The largest torque terms occur near cusps in the Wulff plots (up to 20% γ_S near cusps in Ni), but in regions away from the cusps, the torque terms are quite low (<2% γ_S , >5° from cusp in nickel).[8] The curvature in Fig. 5 of the Ni/NiO interfaces is reasonably constant with no sharp changes in the morphology, so it is believed that the energy measured will be representative of an average value over a wide angular range, but with little variation in curvature the derivatives or torque terms are considered small. When torque terms in Fig. 5 are neglected the relative energies of the two Ni/NiO interfaces written in terms of the energy of the high angle Ni grain boundary are as follows:

$$\gamma^{(1)}(Ni/NiO) = 1.16 \gamma(Ni-gb), \quad \gamma^{(2)}(Ni/NiO) = 1.12 \gamma(Ni-gb)$$

A second triple grain junction is shown in Fig. 6a for the case with a NiO grain boundary intersecting two Ni/NiO interfaces. The NiO grain boundary is a 1.8° tilt boundary [(110) plane with (001) tilt axis]. The edge dislocations with Burgers vectors $\frac{1}{2}[110]$ and average spacing 9.2nm are shown in Fig. 6c. There is also interface structure in one of the Ni/NiO boundaries as seen under the higher magnification of Fig. 6b. In this example the orientation of the NiO gb is near a $\Sigma = 1$ cusp in the Wulff plot for the two NiO grains, therefore torque terms are likely to be important and are included in the solution to Herring's equilibrium equation. In this case the relative energies of the Ni/NiO interfaces are as follows:

$$\gamma^{(1)}(NiO/Ni\text{-torque term of Ni/NiO interface}) = 0.85\{\gamma(NiO\text{-low angle gb})\text{-torque term}\}$$

$$\gamma^{(2)}(NiO/Ni) = 1.34\{\gamma(NiO\text{-low angle gb})\text{-torque terms}\}$$

The torque terms are omitted from $\gamma^{(2)}(Ni/NiO)$ for the reasons discussed in the previous example. Judging from these ratios of energies and values of Ni and NiO grain boundary energies from ref. 8&9, the Ni/NiO interfacial energies are roughly in the neighborhood of 1000 mJ/m² with interfaces such as in Fig. 6b being probably 75% of this value. The possible range of values for these interfacial energies will be better documented and a more comprehensive analysis performed as further experimental values are reported. Oxidation stresses and growth anisotropy may influence the oxide grain orientations and hence the type of boundaries impinging upon triple grain junctions, but their influence on energy measurements per se is considered minor since boundary curvature to establish equilibrium dihedral angles is quite localized.

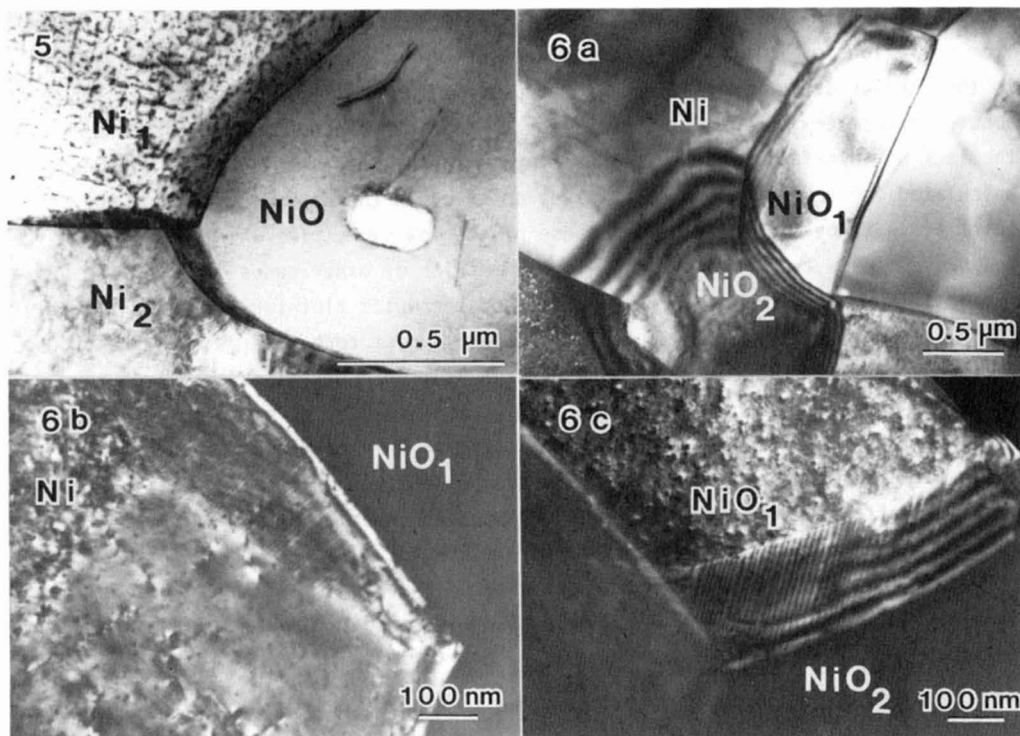


Fig. 5 - Triple grain junction with Ni grain boundary.

Fig. 6-(a) Triple grain junction with NiO grain boundary;
 (b) higher mag. of Ni/NiO interface structure;
 (c) higher mag. of edge dislocations in NiO tilt boundary.

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