From Alloy to Oxide: Capturing the Early Stages of Oxidation on Ni-Cr(100) Alloys

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SUPPORTING INFORMATION

S1. Bandgap measurements for STS Spectra

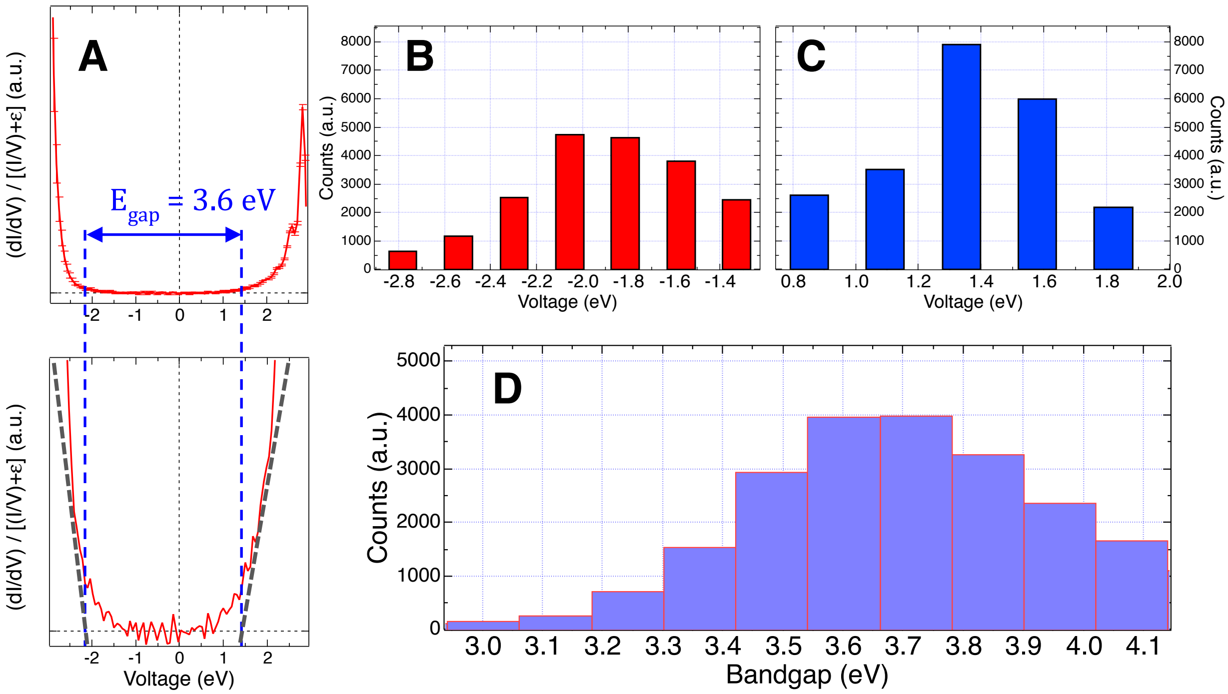


Figure-S1. (A) The cross-point of the tangent is used for determining the bandgap from STS data. The averaged STS curves (approx. 50 curves) were taken from NiO grown on Ni-12wt.%Cr. Distributions of the valence (B) band and conduction (C) band maxima and minima are computed from the STS spectra by numerically computing the voltage at which the current is above the threshold value reported in the method section. The bandgaps (D) are also acquired from the numerical differentiation routine and are in great agreement with the max/min of the valence/conduction bands.

This report uses the tangent method to establish specific bandgaps. This method relies on taking the derivative of the conduction and valence bands edges, and extending the slope across the x-axis. Statistical information regarding the edges of the conduction and valence bands yielded a bimodal distribution around 1.5 eV and -2.1 eV respectively, indicating that the tangent method was best suited for describing this surface. However, given the nature of room-temperature STS taken, absolute gaps are neither claimed nor suggested. Instead, relative differences in the electronic structure between various surface features are used as a measure of distinction.

S2. Ni-12%Cr metal surface topography of measurement at low V_{bias}

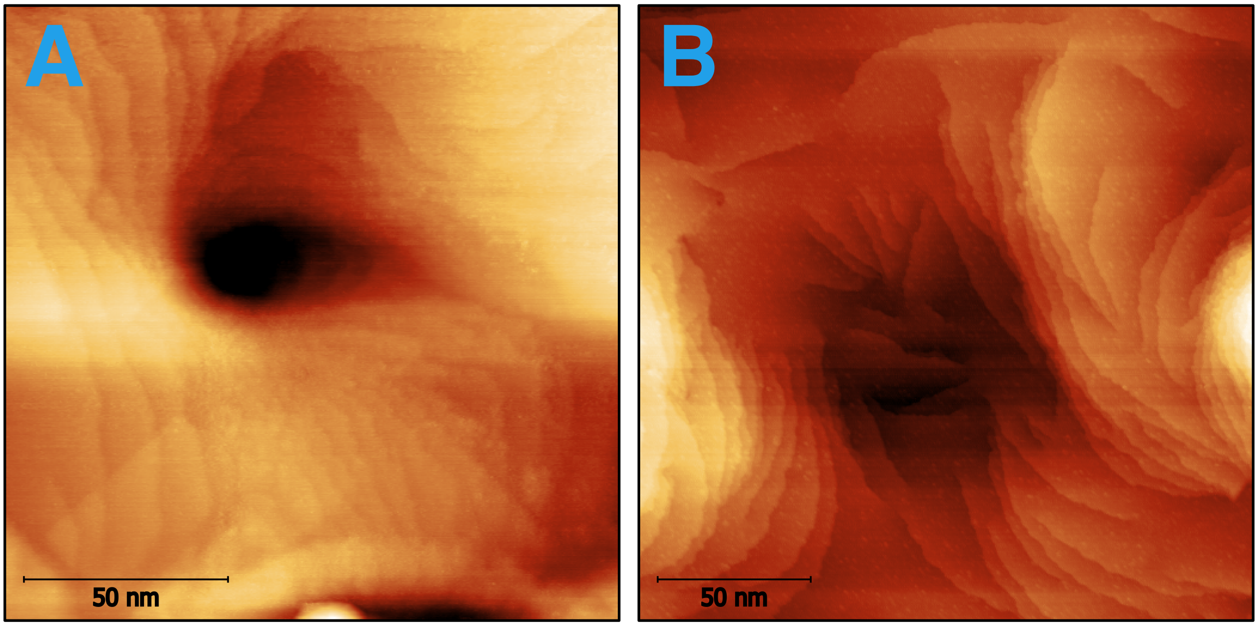


Figure-S2. STM image, both taken at 0.15V and 0.1 nA, of (A) Ni-12wt.%Cr before oxidation and (B) the same alloy after 7L + 600 °C anneal.

The distinct and highly preferential step edge faceting observed post oxidation is no longer present after the crystalline NiO has been thermally removed by the 600 °C anneal. Given the metal surface's circular terraces, one would expect Ni-Cr to have a relatively isotropic interfacial energy. Once the NiO was removed, removed, the surface would have lacked the surface energy curvature necessary to facilitate faceting, thus driving the surface to relax back to a similar orientation with round terraces.

S3. Image Data Processing and Correction

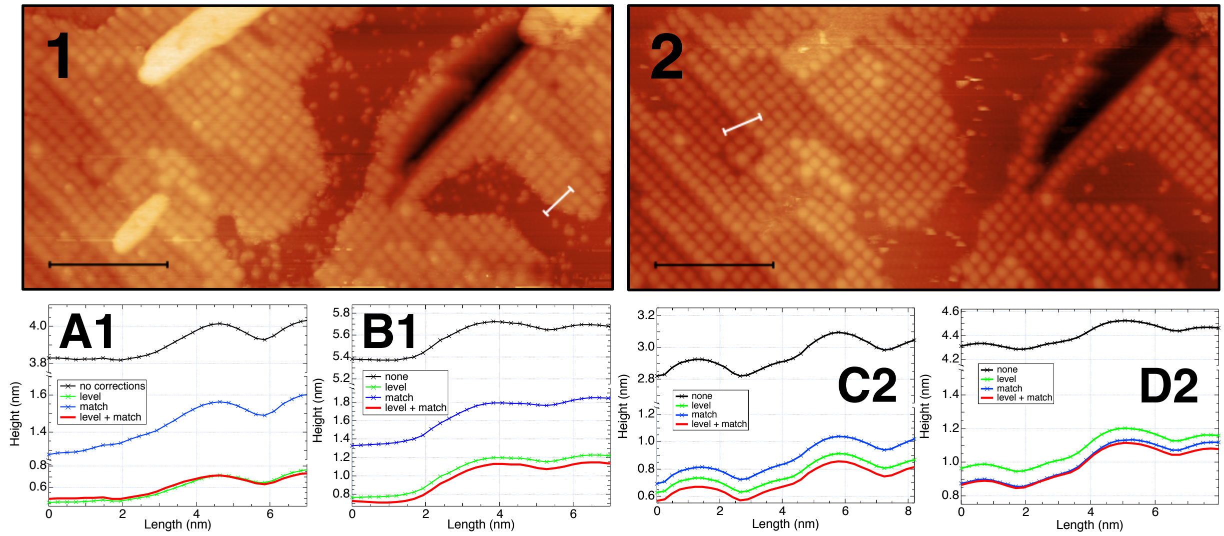


Figure-S3-(1-2). The measured step height of 1^{st} - Layer-NiO at (A) -3.0 V and 0.1 nA and (B) 3.0 V and 0.1 nA. The image 1 was taken at the positive bias, while image 2 was taken at negative bias. Both scale bars are 25 nm.

The plots show the different correction methods in Gwyddion[1] used to establish the most appropriate measure of apparent step height between the 1^{st} layer and NiO. To improve the overall visual quality of the images, the reported values in this paper were taken after plane leveling* and feature matching** were employed. As seen by the line profiles, no significant changes in the apparent step heights were observed after post processing. Significant deviations where observed if linescans were taken over large portions of the image, but as shown above smaller and more localized scans were used in the collection of apparent height data. The numerical values for the apparent heights reported in this work were taken from the difference between the surface features above and below a particular line scan, i.e. maximum to maximum.

* Leveled points are identified on the image; a plane between points is generated and subtracted from the data.

**A representative height for each scan line (along the horizontal direction) is found and is subtracted from the background.

S4. Apparent Height, and Periodic Rows in Oxide Nodules

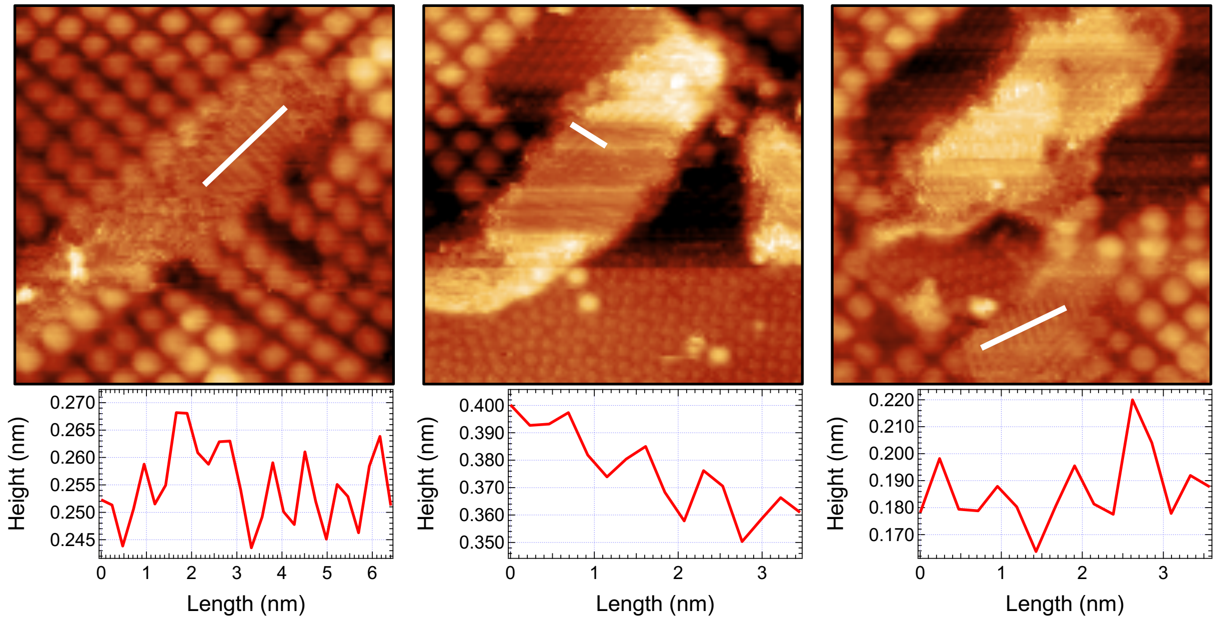


Figure-S4.1. Images of the oxide nodules taken at -3.0 V and 0.1 nA. Lines scans were performed across the periodic rows visible in parts of the nodules. Height vs. length of each respective profile were plotted to ascertain the peak distances between the rows.

At negative tip bias the filled states of the oxide nodules were probed and ordered rows were observed. Linescans were taken and the statistical average peak spacing was found to be 0.84 ± 0.03 nm. The lattice constant of the the spinel oxide, $NiCr_2O_4$, has been experimentally and theoretically determined to be 0.83 ± 0.07 nm.[2] Given this similarity and their characteristic surface position, never isolated from the NiO nor the phase separated Cr, it is possible that these nodules are the spinel. However, our current experimental techniques cannot confirm the specific nature of these nodules.

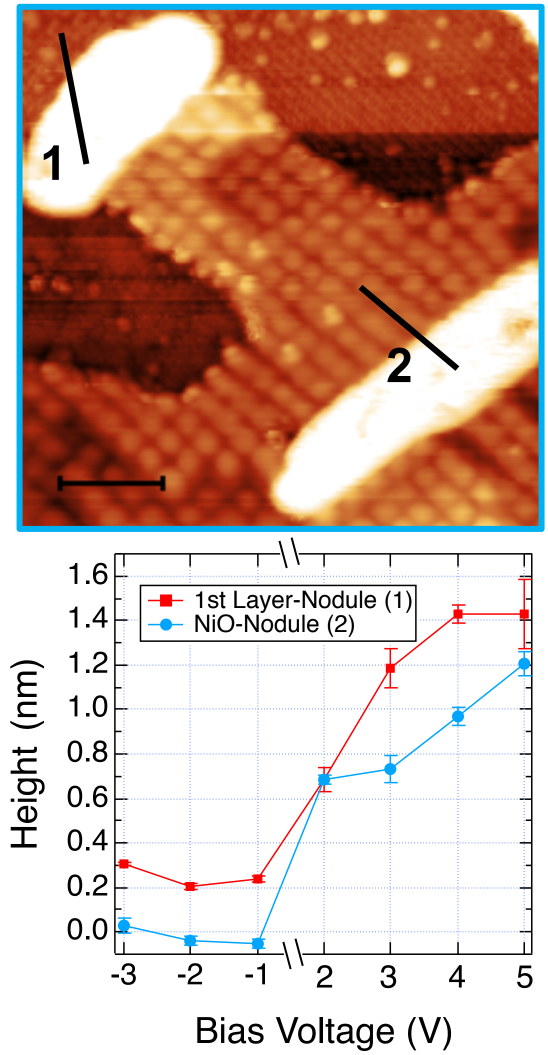
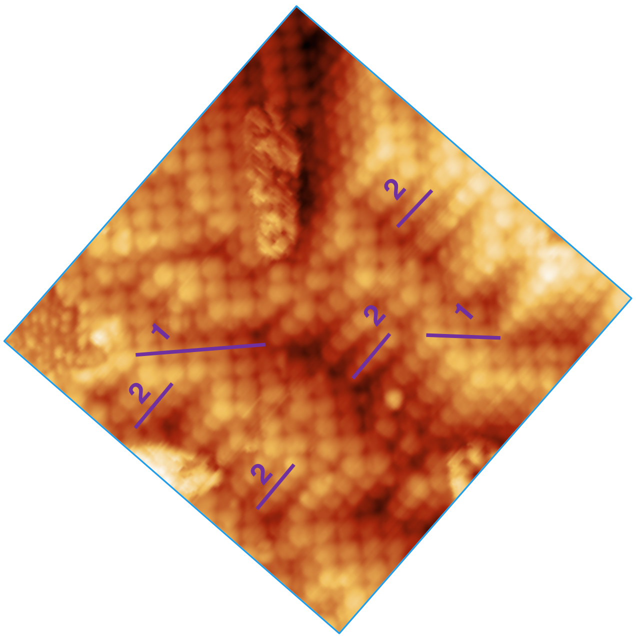


Figure-S4.2. The apparent step heights between the 1st layer and the oxide nodules (line profile 1) and the NiO and the oxide nodule (line profile 2). The image was taken at 3.0 V and with a constant tunneling current of 0.1 nA. The scale bar is 10 nm.

Linescans of the oxide nodules reveal that when a negative tip bias is used, the nodules appear as depressions when measured from the NiO to the nodule (line profile 2) and as 0.25 nm protrusions when the apparent height is measured from the 1st layer Ni-Cr-O surface (line profile 1). When positive tip bias is applied, there is a relatively linear increase in apparent height, which reaches a maximum of 1.4 ± 0.18 nm. It is likely that these nodules have reached a limiting thickness, and are this stage of the oxidation have begun to propagate laterally as there is a range in length of nodules varies from 10 nm up to 50nm, but all with relatively similar apparent heights.

S5. Coincidence Lattice – Measurement of NiO Periodicity on Terrace and Wedge



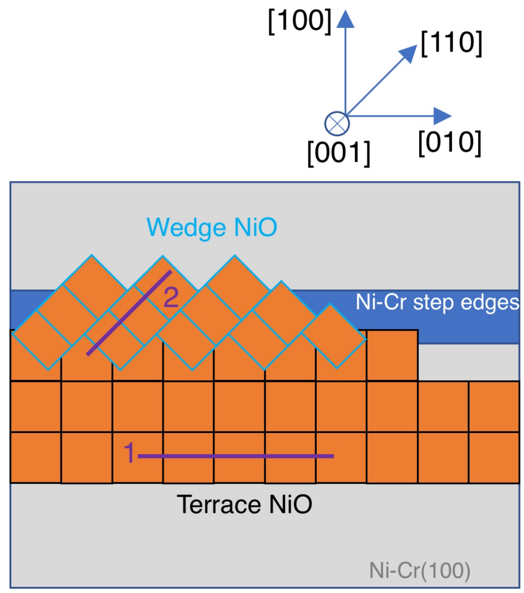


Figure-S5. Illustration of measurement of coincidence lattice on terrace (linescan in direction 1), and at step edges (linescan in direction 2). A few lines corresponding to 1 and 2 are icnluded as examples in the image on the left hand side.

This figure illustrates the surface crystallography as it pertains to the measurement of coincidence lattices on the terrace and the step edges. All linescans within the NiO lattice are measured edge-to-edge with respect to the repeat unit in the NiO. The image is identical to Figure 5.B in the main body of the manuscript and rotated to align line 1 and 2 to the schematics on the right hand side. Line 1 is parallel to the [010] or equivalent [100] direction, and line 2 is parallel to the [110] direction.

References

(1) Nečas, D.; Klapetek, P. Gwyddion: An Open-Source Software for SPM Data Analysis. *Open Phys*. **2011**, *10* (1), 181–188.

(2) Brik, M. G.; Suchocki, A.; Kamińska, A. Lattice Parameters and Stability of the Spinel Compounds in Relation to the Ionic Radii and Electronegativities of Constituting Chemical Elements. *Inorg. Chem*. **2014**, *53* (10), 5088–5099.