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Nanoscopic nickel aluminate spinel ($NiAl_2O_4$) formation during NiAl(1 1 1) oxidation

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Abstract

Oxidation of a NiAl(1 1 1) single crystal surface was investigated using high resolution soft X-ray photoelectron spectroscopy (HRSXPS), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray spectroscopy (EDS), X-ray mapping, and atomic force microscopy (AFM). After repeated oxygen exposure, annealing, and cleaning cycles under ultrahigh vacuum conditions, a new oxide phase in the form of tiny 3-dimensional surface structures was detected. These features are several micrometers long and ~300 nm high and oriented along low index $\langle\bar{1}01\rangle$ directions in the plane of the substrate; they have nickel aluminate spinel ($NiAl_2O_4$) stoichiometry. We propose that repeated cycles of oxygen dosing and annealing of the NiAl(1 1 1) surface leads to oxygen diffusion into the bulk and nucleation of spinel below the surface.

Keywords: Nickel aluminum; Spinel; Oxidation; Soft X-ray photoelectron spectroscopy; Nucleation; Faceting

NiAl is a well-known oxidation resistant material, and oxidation of its surfaces has been investigated for several decades. Particular interest has focused on the NiAl(1 1 0) and NiAl(1 0 0) surfaces that are model substrates for growth of thin films of aluminum oxide used in catalyst studies [1].

In comparison with (1 0 0) and (1 1 0) planes of NiAl [2–8], little work has been reported on the oxidation of NiAl(1 1 1) [3]. The NiAl(1 1 1) surface is a good candidate for facet formation due to its atomic-scale roughness. Consistent with our previous studies of faceting on morphologically unstable and atomically rough transition metal surfaces [9–11], oxygen-covered NiAl(1 1 1) changes its morphology and forms facets upon annealing [3]. During our studies of facet formation (to be described elsewhere [12]), the NiAl(1 1 1) sample was frequently exposed to oxygen and annealed to high temperatures (up to 1500 K). We have found that repeated prolonged exposure to oxygen followed by annealing of NiAl(1 1 1) leads to the formation of microscopic 3-dimensional oxide features that "erupt" from the surface.

In this article, we report our characterization of these unusual oxide structures using HRSXPS, EDS X-ray mapping, SEM, and AFM.

A NiAl single crystal with (1 1 1) orientation was obtained from MaTeck; its orientation was confirmed by X-ray diffraction (XRD). The crystal (10 mm in diameter and of 1 mm thick) was spot-welded to a tantalum holder via tantalum wires. The sample temperature was monitored by a C type (W–5 at.% Re/W–26 at.% Re) thermocouple spot-welded directly to the back of the crystal. The NiAl(1 1 1) surface was cleaned under ultrahigh vacuum (UHV) conditions by repeated cycles of Ar ion sputtering and annealing to ~1400 K. The cleaning process was repeated until the main contaminants, carbon and oxygen, could no longer be detected with Auger spectroscopy (AES) or HRSXPS.

NiAl(1 1 1) surface oxidation was performed under UHV conditions with base pressure less than $\sim 1 \times 10^{-10}$

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Torr. Al 2p and Ni 3p core level peaks were characterized with HRSXPS on beamline U4A at the national synchrotron light source (NSLS). The photon energy used was 150 eV, and the total instrumental resolution was 127 meV. A VSW hemispherical energy analyzer of 100 mm mean radius and 5° angular acceptance angle collected normally-emitted photoelectrons with a pass energy of 5 eV.

For high resolution imaging, the sample was transferred in air to the field emission scanning electron microscope (ZEISS Gemini 982) chamber. The ZEISS 982 objective lens and the Gemini in-lens SE detector are described in detail elsewhere [13]. The probe size of the electron beam in these experiments is ~2 nm at 2.5 keV energy. The experimental resolution limit of the HRSEM using secondary electrons is less than 10 nm at 2.5 keV. This accelerating electron beam energy was chosen to optimize spatial and depth resolution for imaging and chemical analysis using X-ray energy dispersive spectroscopy (EDS). An integrated imaging and EDS analyzer made by Princeton gamma-tech (PGT) was used for image processing and X-ray mapping. An air operated AFM Q-Scope^{TM} 250 was also used to investigate the morphology of the sample surface.

The main point of the present report concerns the formation and growth of 3-dimensional oxide features on NiAl(1 1 1). Background experiments based on LEED, HRSXPS and AES are as follows.

When clean NiAl(1 1 1) is exposed to oxygen at room temperature, amorphous oxide develops on the surface. A crystalline alumina film forms after annealing the oxygen-covered surface in the temperature range 900 K to 1050 K. The atomically rough NiAl(1 1 1) surface remains planar at room temperature when exposed to oxygen. However, the oxygen-covered surface changes its morphology and develops facets upon annealing at ~1100 K. Following annealing above 1250 K, the O/NiAl(1 1 1) surface becomes planar again. In the case of soft XPS (see Fig. 1a), upon oxygen deposition at room temperature, the Al^0 2p metal doublet peaks at binding energy 72.5 eV and 72.9 eV are broadened and attenuated, and a new peak appears at binding energy 75.4 eV, which is associated with aluminum oxide formation. This Al^{3+} 2p feature persists until ~1100 K and then finally disappears upon annealing to more than 1250 K. After further annealing up to 1400 K, the aluminum oxide film is no longer detected with any surface sensitive techniques, such as HRSXPS, LEED and AES; this indicates that oxygen desorbs and/or diffuses into the bulk at elevated temperatures.

After several months of repeated oxidation and heating, the cleaning procedure became less effective and oxygen contamination remained on the surface. A new form of oxide was detected with HRSXPS; the appearance of a new peak shifted by 1 eV to higher binding energies is observed (see Fig. 1b). Under these conditions, oxygen could not be removed from the surface by heating alone. HRSXPS data indicate that the Al^{3+} peak is present at all annealing temperatures up to 1400 K rather than disappearing at temperatures above 1250 K, as happens at earlier stages of NiAl(1 1 1) oxidation treatments.

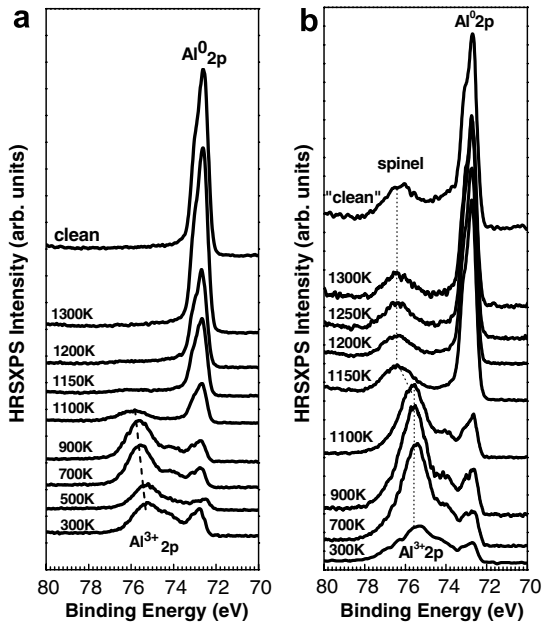

Fig. 1. HRSXPS spectra of oxygen-dosed NiAl(1 1 1) taken at normal emission at a photon energy 150 eV: (a) dose 300 L prior to annealing, early stages of oxidation; (b) dose 200 L, after repeated exposure to oxygen and annealing. In each case, the sample is annealed to the indicated temperature for 60 s and then cooled to 300 K for measurements.

At the later stages of oxidation, the crystal surface lost its shine and became milky-looking; it appeared the surface had roughened microscopically. Upon removal from vacuum and characterization by SEM and AFM, 3-dimensional dendritic features are detected on the surface (see Figs. 2 and 3); their dimensions are several micrometers in length, and 250–400 nm high. This remarkable uniformly-distributed "eruption" of 3-dimensional features exhibits 3-fold symmetry with "arms" oriented along low index$\langle\bar{1}\,0\,1\rangle$ directions in the plane of the substrate.

To provide insights into the chemical composition of the dendritic structures, X-ray EDS measurements and elemental mapping were performed. Fig. 4a shows X-ray emission maps from oxygen K and nickel L peaks. All regions where features occur are rich in oxygen compared to the substrate. In order to optimize the depth and spatial resolution, the measurements were carried out at a low incident electron energy of 2.5 keV. A Monte Carlo simulation was performed to determine spatial resolution in EDS of spinel [14]. By following electron trajectories and energies, we obtain a 2-dimensional map showing where the X-rays originate. This shows that the detected X-rays are collected from a depth of ~80 nm and the lateral resolution is ~10 nm, which is much less than the dimensions of features on the surface. Pronounced peaks of oxygen, nickel and aluminum are seen in EDS spectra (see also Fig. 4b). To eliminate charging problems, a thin carbon film ~20 Å thick was deposited on the surface. Based on the intensity ratios (Ni:Al:O) in the SEM X-ray mapping study, the