BNL-113577-2017-JA

**A Comparative Study of Oxidation of NiAl(100) by
Molecular Oxygen and Water Vapor Using Ambient-
Pressure X-ray Photoelectron Spectroscopy**

**Qianqian Liu, Hailang Qin, Jorge
Anibal Boscoboinik, and Guangwen Zhou**

Submitted ACS - Langmuir

October 2016

Center for Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

A Comparative Study of Oxidation of NiAl(100) by Molecular Oxygen and Water Vapor Using Ambient-Pressure X-ray Photoelectron Spectroscopy

Qianqian Liu¹, Hailang Qin¹, Jorge Anibal Boscoboinik², and Guangwen Zhou^{1*}

¹Department of Mechanical Engineering & Multidisciplinary Program in Materials Science and Engineering, State University of New York, Binghamton, NY 13902

²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

Abstract

The oxidation behavior of NiAl(100) by molecular oxygen and water vapor under a near-ambient pressure of 0.2 Torr is monitored using ambient pressure X-ray photoelectron spectroscopy. O₂ exposure leads to the selective oxidation of Al at temperatures ranging from 40 °C to 500 °C. In contrast, H₂O exposure results in the selective oxidation of Al at 40 °C and 200 °C, increasing the oxidation temperature above 300 °C leads to simultaneous formation of both Al and Ni oxides. These results demonstrate that O₂ oxidation forms a nearly stoichiometric Al₂O₃ structure that provides improved protection to the metallic substrate by barring the outward diffusion of metals. In contrast, H₂O oxidation results in the formation of a defective oxide layer that allows outward diffusion of Ni at elevated temperatures for simultaneous NiO formation.

*To whom correspondence should be addressed: gzhou@binghamton.edu

1. INTRODUCTION

NiAl is a technologically important intermetallic material possessing a high melting point, low density, good oxidation/corrosion resistance, and metal-like electrical and thermal conductivities. The thin aluminum oxide film grown by selective oxidation of Al in the NiAl alloy is widely used as one of the most important supports for dispersed metal catalysts.¹⁻⁵ Due to these important industrial applications and also the fundamental importance in understanding the degradation mechanism of intermetallic alloys, the initial-stage oxidation of single-crystal NiAl(100) has been extensively studied to address the atomistic mechanism of the formation of ultrathin aluminum oxide films using a wide range of surface science tools including low-energy electron diffraction (LEED)⁶⁻¹¹, X-ray photoelectron spectroscopy (XPS)¹¹⁻¹³, electron energy loss spectroscopy^{6,7}, scanning tunneling microscopy (STM)^{8-11, 14-16}, and low-energy electron microscopy (LEEM)^{10, 16}. These surface science studies of the oxidation of NiAl are performed mostly under ultrahigh vacuum (UHV) conditions with carefully dosing small amounts of oxygen gas. While the surface science approach has been very successful in many cases as shown in aforementioned studies, the pressure gap between surface science experiments and technological relevant oxidation processes that often take place within high temperature and high pressure regimes prevents the direct extrapolation of the knowledge obtained from the idealized condition. This is because the structure and composition of the surface can drastically change when going from UHV to realistic situations. Therefore, the effects of temperature and pressure must be properly accounted for in order to obtain a reliable description of the surface structure/chemistry and transformations under the technologically relevant conditions.

Recent advances in instrumentation have made it possible to investigate gas-surface reactions under realistic pressures with *in situ* measurements. Particularly, X-ray photoelectron spectroscopy (XPS) has evolved dramatically in recent years with the implementation of differential pumping schemes that allow for the investigation of surface reactions on the atomic scale at the gas pressure of up to ~ 1

Torr.¹⁷⁻²¹ Since the formation of an oxide layer on the metal surface is expected to change dramatically its chemical properties, employment of these *in situ* techniques for oxidation studies will provide unique opportunities to establish the principles of controlling atomic processes of surface oxidation via manipulating the thermodynamic and kinetic variables of the reaction including temperature, oxygen pressure, surface orientation and morphology, and alloying.

In ambient conditions, the reaction of NiAl with oxygen or an oxygen-containing atmosphere such as water vapor results in the selective oxidation of Al. The reaction proceeds with the initially rapid growth of a thin aluminum oxide layer followed by an abrupt reduction in the oxidation rate, thereby reaching a limiting thickness of the oxide film. Compared to the extensive study on the oxidation of a clean metal surface, the fundamental understanding of the effect of such a passivation oxide layer on the subsequent oxidation at elevated temperatures has not been addressed. In this work, we report an *in situ* study of the oxidation of NiAl(100) in a more practical oxidation condition, namely an ambient gas pressure with the ambient pressure X-ray photoelectron spectroscopy (AP-XPS). We perform a comparative study of the oxidation of NiAl(100) with molecular oxygen and water vapor at the near ambient pressure of 0.2 Torr with a stepwise increase in temperature from 40 °C to 500 °C. With the temperature increase in such a stepwise manner, our experiments here allow for examining the oxidation behavior of a surface covered with a pre-existing oxide film that forms at a lower temperature and resembles the presence of a native oxide layer. The use of molecular oxygen and water vapor as the oxidizing species allows for elucidating how the growth and properties of the oxide film depend on the oxidizing atmosphere, which has been rarely addressed at the atomic scale under such a high pressure.

2. EXPERIMENTAL

The AP-XPS experiments were performed in an ambient-pressure X-ray Photoelectron Spectroscopy (AP-XPS) chamber equipped with a SPECS Phoibos 150 analyzer and an Ar-ion sputtering

gun at beamline X1A1 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The AP-XPS system is equipped with several differential pumping stages between the reaction chamber and the hemispherical analyzer which results in different gas pressures in these two chambers, i.e., up to several Torr in the reaction chamber but remaining ultrahigh vacuum conditions (lower than 10^{-7} Torr) in the analyzer. Photo-emitted electrons leave the high-pressure chamber through a small aperture into the multi-stage differentially pumped electron energy analyzer that allows for continuously collecting XPS signals from the sample enclosed in the elevated pressure volume. The XPS spectra of gas phases (O_2 and H_2O) can be observed at the pressure > 0.1 Torr. The photon energy range of the beamline is from ~ 200 eV to ~ 850 eV, which covers the O 1s, C 1s, Al 2p and Ni 3p core levels. An Au foil in the XPS chamber was used to calibrate the real incident photon energy for acquiring XPS data. In the O_2 oxidation experiment, the real incident photon energy was 707 eV. The H_2O oxidation experiment was performed a few months later and the real incident photon energy was 683 eV because of the change in the positions of the motors that drove the monochromator. Spectra of Ni 3p, Al 2p, and O 1s were acquired *in situ* during the oxidation.

The NiAl(100) single crystal purchased from Princeton Scientific Corp, was a top-hat-shaped disc (1 mm in thickness and 8 mm in diameter) and cut to within 0.1° to the (100) crystallographic orientation and polished to a mirror finish with a purity of 99.9999%. The NiAl(100) crystal was cleaned by repeated cycles of Ar ion sputtering (1×10^{-5} Torr, 1 keV) at room temperature and annealing at 750°C for about 10 min, until no carbon was detected by XPS. However, a small amount of oxygen was still present as detected in O 1s XPS spectra and cannot be completely removed, likely due to the relatively high base pressure of the XPS chamber (the presence of such residual oxygen had negligible impact on the oxidation experiments performed at the near ambient condition). Sample temperature was measured with a K-type thermocouple. A separate system equipped with the capabilities for surface structure characterization, i.e., low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM),

was used to check the surface quality of the NiAl(100) prepared using the same sputtering and annealing procedure as the AP-XPS experiments. The as-cleaned surface showed sharp diffraction spots of the $c(3\sqrt{2} \times 3\sqrt{2}, \sqrt{2} \times 3\sqrt{2})R45^\circ$ reconstruction^{15, 22} and appeared as flat terraces separated by atomic height steps.

High purity oxygen gas was directly introduced to the XPS chamber through a variable-pressure leak valve to oxidize the freshly cleaned NiAl(100). Water (18.2 M Ω) was put into a glass flask (ACE) and further purified with several freeze–pump–thaw cycles before dosing through a separate variable-pressure leak valve. Ion gauges were used to measure the gas pressures. The effect of the ion gauge sensitivity correction was not accounted for during the pressure measurements because of the minor difference in the gas correction factors for O₂ and H₂O. No carbon contamination was detected by XPS from the O₂ and H₂O exposures. The freshly-cleaned surface was exposed to O₂ or H₂O at the pressure of 0.2 Torr first at T = 40 °C, followed by the stepwise temperature increase to 200 °C, 300 °C, and 500 °C during the gas exposure. Under each condition, the surface was oxidized to a saturated thickness of the oxide film, unless noted otherwise. After the oxidation at 500 °C, the chamber was then evacuated and the sample was annealed respectively at 500 °C and 750 °C in vacuum to investigate the temperature effect on the atomic structure of the oxide film. The conditions for oxidation and subsequent vacuum annealing are detailed in Table 1.

At each temperature during the gas exposure and annealing, the XPS O 1s, Ni 3p, and Al 2p spectra were acquired at 10 min, 20 min, and 30 min or longer as required. Each spectrum was fitted with a Shirley background subtraction. The binding energy extracted is estimated to have an error of less than 0.05 eV. The thickness of the oxide film was calculated using the ratio of the total oxidic Al³⁺ 2p and metallic Al⁰ 2p peak areas in each single XPS spectrum of the oxidized NiAl(100) surface, assuming a uniform oxide layer and is estimated to have an error of less than 1 – 2 Å.^{22, 23} The inelastic mean free path λ is estimated by the kinetic energy of Al 2p that depends on the incident photon energies. In the

O₂ oxidation experiments, $\lambda \approx 11.3 \text{ \AA}$ for the incident photon energy of 707 eV; in the H₂O oxidation experiments, $\lambda \approx 10.8 \text{ \AA}$ for the incident photon energy of 683 eV.²⁴ This indicates that the small difference in the incident photon energies (24 eV) used in acquiring the XPS data during the O₂ and H₂O oxidation has negligible effect on the detectable oxide thicknesses (less than 1 Å). The binding energy scale was calibrated by measuring Fermi edge spectra of Ni. The peak intensities were normalized by the highest intensity value in each spectrum. The intensities of the spectra between different oxidation temperatures were not compared because the photoelectron counts can be affected by gas phase molecules.¹⁷

3. RESULTS

3.1. Oxidation by molecular oxygen

The freshly cleaned NiAl(100) surface was first oxidized by oxygen gas at $p(\text{O}_2) = 0.2 \text{ Torr}$ and temperatures ranging from $T = 40 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$. Figs. 1(a, b) show the evolution of the XPS spectra of O 1s and Al 2p/Ni 3p regions during the oxidation with the conditions given in Table 1. The oxide film reached its limiting thickness after the O₂ exposure at each T. As seen in Fig. 1(a), the O 1s region shows a very low intensity peak for the freshly clean NiAl(100) surface, which can be attributed to the residual oxygen that cannot be completely removed by sputtering and annealing due to the relatively high base pressure ($\sim 7 \times 10^{-9} \text{ Torr}$) of the chamber. This can also be evidenced by the small intensity of the Al³⁺ 2p peak in the corresponding Al 2p spectrum obtained from the freshly cleaned NiAl(100) surface (Fig. 1(b)). After exposure to $p(\text{O}_2) = 0.2 \text{ Torr}$ with the stepwise temperature increase from $40 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$ with the holding time of 30 min for each T, the O 1s spectra show a clear trend of increase in the binding energy (BE).

Fig. 1(b) shows the corresponding XPS spectra in the Al 2p/Ni 3p regions. It can be seen that the binding energies of the metallic Ni⁰ 3p and Al⁰ 2p do not show any noticeable shift with the temperature

increase. However, the binding energy of the Al^{3+} 2p peak shows a clear shift to a higher binding energy. This is also qualitatively consistent with the studies on thermal oxidation of aluminum²⁵ and our earlier results on NiAl(100) under the UHV conditions of O_2 exposure¹³. Also, it is worthwhile to note that the intensities of the metallic Ni^0 3p and Al^0 2p peaks diminish and disappear completely at 500 °C, while the peak intensity of the Al^{3+} 2p peak is very strong, indicating that the oxide film has reached a certain thickness at which the metallic peaks are completely attenuated. The oxide film showed stepwise increase in its thickness with the stepwise increase in temperature and reached about 22 Å after the oxygen exposure at 300 °C, as shown in Table 2. The thickness after oxidation at 500 °C is even larger but is not estimated here, because the metallic Al^0 2p is completely attenuated.

As can be seen in Fig. 1(a), the O 1s peak from O_2 exposure at 40 °C is well fit by two components at the BE = 532.4 eV and 531.3 eV. The 532.4 eV component is in good agreement with the reported values of O in amorphous Al_2O_3 ^{20, 26, 27}, while the lower BE one at 531.3 eV is attributed to O from interfacial aluminum oxide which can be assigned as Al-deficient AlO_x ^{20, 27, 28}. As seen in Fig. 1(a), the oxide consists of mainly AlO_x and a small amount of Al_2O_3 , after O_2 exposure at 40 °C. However, the peak corresponding to AlO_x at BE = 531.3 eV has disappeared after the oxidation at 200 °C, indicating that the AlO_x component is completely converted to the more stoichiometric Al_2O_3 component. After O_2 exposure at $T = 300$ °C, another peak at a higher binding energy of 533.3 eV arises. This peak is assigned to the O in the crystalline Al_2O_3 ($\gamma\text{-Al}_2\text{O}_3$), which is 0.9 eV higher than the BE of the amorphous Al_2O_3 , in good agreement with the reported difference (0.5 – 1.0 eV) between the amorphous Al_2O_3 and $\gamma\text{-Al}_2\text{O}_3$.^{25, 29} When the temperature is further increased to 500 °C, the amount of amorphous Al_2O_3 component decreases while the amount of $\gamma\text{-Al}_2\text{O}_3$ increases, indicating more amorphous Al_2O_3 is crystallized to form $\gamma\text{-Al}_2\text{O}_3$. The binding energies of the various O components are summarized in Table 2.

The identification of the different aluminum oxides from the O 1s spectra is also confirmed from the Al 2p spectra shown in Fig. 1(b). After O_2 exposure at 40 °C, the Al^{3+} 2p peak is deconvoluted into

two components, one at BE = 74.4 eV which can be attributed to AlO_x ^{20,27}, and the other one at BE = 75.6 eV attributed to the amorphous Al_2O_3 ^{20,27}. After the oxidation at 200 °C, the peak (BE = 74.4 eV) corresponding to AlO_x completely disappears. The Al^{3+} 2p peak is well fit by only one component at BE = 75.6 eV, which corresponds to the more stoichiometric amorphous Al_2O_3 . When the temperature is increased to 300 °C and above, the Al^{3+} 2p peak is well fit by two components, one at BE = 75.6 eV corresponding to the amorphous Al_2O_3 , and the other one at BE = 76.4 eV corresponding to $\gamma\text{-Al}_2\text{O}_3$.^{25, 30}

Both the O 1s and Al^{3+} 2p peaks shift to higher binding energies with further increasing the oxidation temperature to 300 °C and then to 500 °C. Such shifts to the higher binding energies at the higher oxidation temperatures are further confirmed by the subsequent vacuum annealing of the as-oxidized sample. Figs. 2(a, b) show spectra taken in vacuum at the corresponding annealing temperatures of the O 1s and Al 2p regions of the as-oxidized sample (right after the oxidation at 500 °C), which show that both the O 1s and Al^{3+} 2p peaks shift only slightly after annealing at 500 °C for 30 min, as expected for aluminum oxide, since the oxide film is grown at 500 °C. However, the binding energies have shift by about 0.2 - 0.3 eV after further annealing at 750 °C for 30 min. This again confirms that the higher oxidation/annealing temperature results in the higher binding energies of the O 1s and Al^{3+} 2p peaks induced by the ordering of the amorphous oxide film. The shifts of the binding energies of the O 1s and Al^{3+} 2p are summarized in Fig. 2. Similarly, as shown in Fig. 2, both the O 1s and Al^{3+} 2p peaks can be deconvoluted into 2 peaks, one corresponding to amorphous Al_2O_3 having binding energies of 532.4 eV (O 1s) and 75.6 eV (Al^{3+} 2p)^{25, 29, 30} and the other corresponding to $\gamma\text{-Al}_2\text{O}_3$ with the binding energies of 533.3 eV (O 1s) and 76.4 eV (Al^{3+} 2p)^{25, 29, 30}. The evolution of the relative intensities of the two peaks (Fig. 2) shows that the amorphous Al_2O_3 is being gradually crystallized while annealing at the elevated temperatures. The shift of the binding energies of the O 1s and Al^{3+} 2p peaks can be attributed to the structure ordering (crystallization) in the aluminum oxide film as the temperature increases. The structure evolution of the NiAl(100) surface and the aluminum oxide film was characterized by LEED and

STM in our previous study, which showed that the aluminum oxide film formed at the relative low temperatures ($< 300\text{ }^{\circ}\text{C}$) is amorphous and transforms to a crystalline state upon annealing above $450\text{ }^{\circ}\text{C}$.¹⁰ It should be noted that the oxide film formed under the oxygen pressure (0.2 Torr) is much thicker than oxide films formed under UHV oxidation conditions that usually have a thickness $< 5\text{ }\text{\AA}$.¹³ The larger thickness of the oxide film may facilitate the formation of $\gamma\text{-Al}_2\text{O}_3$ as shown here, rather than the $\Theta\text{-Al}_2\text{O}_3$ phase by UHV annealing of ultrathin aluminum oxide films^{10, 15, 16}. In general, the magnitude of the binding energy shift is known to scale with the number of heterogeneous chemical bonds and a larger binding energy shift can be attributed to a larger coordination number.³¹ The binding energies of O 1s and Al^{3+} 2p of the amorphous aluminum oxide are reported to be about 0.5 – 1.0 eV lower than those of $\gamma\text{-Al}_2\text{O}_3$ on an Al substrate.^{25, 29, 30} With the increase in temperature, more crystalline oxide is developed by ordering the amorphous aluminum oxide, which results in the shifting of both O 1s and Al^{3+} 2p peaks to the higher binding energies.

3.2 Oxidation by water vapor

The NiAl(100) surface cleaned similarly by sputtering and annealing in the AP-XPS chamber was oxidized by H_2O under the same temperature and pressure conditions as O_2 oxidation. Figs. 4(a, b) show the evolution of the XPS spectra of O 1s and Al 2p/Ni 3p regions acquired *in situ* during the oxidation. Compared to the freshly-cleaned surface (Fig. 1), it can be noted from Figs. 4(a, b) that the as-cleaned NiAl(100) surface shows slightly more residual aluminum oxide, as indicated by the slightly stronger Al^{3+} 2p peaks because of the higher base pressure ($\sim 1 \times 10^{-8}$ Torr) of the chamber. The oxide film reached its limiting thickness after H_2O exposure at each T. There is no any noticeable shift in the binding energies of the metallic Ni^0 3p and Al^0 2p with the temperature increase. However, the intensity of the metallic Al^0 2p peak diminishes and disappears completely at $300\text{ }^{\circ}\text{C}$ but the metallic Ni^0 3p peak is still visible (Fig. 4(b)). The aluminum oxide film also shows stepwise increase in its thickness at lower temperatures and

reaches about 15.7 Å after H₂O exposure at 200 °C, as shown in Table 3. The thickness of aluminum oxide film cannot be estimated after the oxidation at 300 °C because the metallic Al⁰ 2p is completely attenuated. However, the non-attenuation of the Ni 3p peak indicates that the diffusion of Ni from the substrate into the oxide film has occurred at the higher T. This is completely different from the O₂ exposure, for which both the metallic Al⁰ 2p and Ni⁰ 3p peaks are completely attenuated at 300 °C, as shown in Fig. 1(b). In contrast, the Ni 3p peak still shows a fair amount of intensity after the H₂O exposure at 300 °C and its relative intensity becomes even stronger from the subsequent H₂O exposure at 500 °C.

As shown in Fig. 4(a), the O 1s peak can be deconvoluted into 3 components with BE = 532.4 eV, 531.3 eV and 533.8 eV, respectively, for H₂O oxidation at 40 °C and 200 °C. As discussed in O₂ oxidation section, the BEs of 532.4 eV and 531.3 eV are related to the amorphous Al₂O₃ and interfacial aluminum oxide AlO_x, respectively. The other peak with the higher BE of 533.8 eV is in good agreement with the reported values of OH species and is related to the O in Al-OH bonds of the aluminum hydroxide.^{26, 32, 33} Also, the peak related to the gas H₂O phase is visible at the higher binding energy of 536 eV. However, the OH peak disappears at 300 °C and above, suggesting the aluminum hydroxide is not stable at the temperature above 300 °C and decomposes into the aluminum oxide, consistent with the previous studies.^{12, 34} Meanwhile, using the binding energies of the amorphous Al₂O₃ and AlO_x peaks does not provide an overall good fitting to the O 1s spectra obtained at 300 °C and 500 °C, and a third peak at a lower BE = 530.3 eV arises. It is unlikely to form the NiAl₂O₄ spinel because the oxidation temperature employed here is far below the formation temperature of the NiAl₂O₄ spinel (~1100 °C in form of bulk spinel structure³⁵ and ~ 900 °C in form of thin film³⁶). The absence of the NiAl₂O₄ phase can also be confirmed from the Al³⁺ 2p, which has a higher BE in NiAl₂O₄ by ~ 1 eV than that in Al₂O₃. As shown in Fig. 4(b), no such BE shift is observed from the Al³⁺ 2p. Therefore, the peak at BE = 530.3 eV is attributed to NiO. This conclusion is also based on the closeness of the O 1s binding energy of the component to

literature data for NiO.^{27, 37, 38} The Ni 2p spectra was not collected to further confirm this conclusion due to the limitation of the beamline, the highest photon energy we can reach was around 700 eV while the BE range for Ni 2p is from 840 eV to 880 eV. However, the O 1s peak at the lower binding energy and the existence of Ni 3p at 300 °C and above provide clear evidence for NiO formation. As shown in Fig. 4(a), the relative intensity for the NiO component increases when the oxidation temperature increases from 300 °C to 500 °C, suggesting the enhanced NiO formation at the higher temperature. This trend is also evidenced from the relatively stronger intensity of the Ni 3p peak at 500 °C than that at 300 °C, as shown in Fig. 4(b).

The effect of annealing temperature on the binding energies of the different oxides is also confirmed by the subsequent vacuum annealing of the H₂O-formed oxide film. Both the O 1s and Al³⁺ 2p peaks shift to the high binding energies (Fig. 5). The O 1s spectra obtained from the as-oxidized sample (after the final H₂O exposure at 500 °C) can be deconvoluted into three components at BE = 532.4 eV, 531.3 eV, and 530.3 eV, which correspond to Al₂O₃ (amorphous), AlO_x and NiO, respectively. The O 1s spectra after the vacuum annealing at 500 °C are quite similar to the as-oxidized sample, except for the stronger peak intensity for the amorphous Al₂O₃ component. Fig. 5(a) shows that a new small peak arises at a higher BE = 533.3 eV after vacuum annealing for 20 min at 750 °C. This peak corresponds to the formation of the crystallized Al₂O₃ (γ -Al₂O₃). It can be also seen from Fig. 5(a) that the relative intensities for NiO and AlO_x peaks decrease after the vacuum annealing at 500 °C and further decreases after the vacuum annealing at 750 °C. This indicates that the defective aluminum oxide (AlO_x) is gradually converted into the more stoichiometric Al₂O₃ upon annealing. Because the heat formation for Al₂O₃ (-1690.7 kJ/mol) is by a factor of seven larger than NiO (-240.8 kJ/mol).^{39, 40} The decrease in the relative intensity of the NiO peak at 500 °C and 750 °C shown in Fig. 5(a) suggests that the NiO component is gradually reduced to Ni via the reaction $\text{NiO} + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Ni}$ upon the vacuum annealing, while the decrease in the relative intensity of the Ni 3p peak at 500 °C and 750 °C shown in Fig. 5(b) is

related to the dissolution of the reduced metallic Ni into the NiAl substrate. Becker et al. also reported similar observation that the NiO formed on Ni₃Al disappeared after annealing above 800 K.⁴¹ The vacuum annealing induced evolution of these oxide components derived from the O 1s spectra (Fig. 5(a)) can be further confirmed from the Al³⁺ 2p and Ni 3p peaks. As shown in Fig. 5(b), the Al³⁺ peak associated with γ -Al₂O₃ shows up after annealing at 750 °C while the relative intensity of the two peaks associated with the defective aluminum oxide (AlO_x) and NiO has dropped upon the vacuum annealing.

The composition of the oxide film can be calculated from the ratio of the relative intensity of the different oxide peaks with respect to the overall O1s spectra. Fig. 6 shows the evolution of the composition of the oxide films formed from O₂ and H₂O exposures and the subsequent vacuum annealing (for convenience of description, the composition of the stoichiometric Al₂O₃ is not further broken down into crystallized and non-crystallized ones). As shown in Fig. 6(a), the O₂-formed oxide film consists initially of both defective aluminum oxide (AlO_x) and stoichiometric aluminum oxide (Al₂O₃). The AlO_x disappears completely at the temperatures above 200 °C. In contrast, the H₂O-formed oxide film is dominated by the defective aluminum oxide AlO_x (Fig. 6(b)), and the composition of the oxide film evolves from (Al₂O₃)_{0.21}(AlO_x)_{0.7}(Al(OH)₃)_{0.09} at 40 °C to (Al₂O₃)_{0.33}(AlO_x)_{0.61}(Al(OH)₃)_{0.06} at 200 °C. Noticeably, increasing the temperature to 300 °C results in the growth of NiO and the composition of the oxide film changes to (Al₂O₃)_{0.27}(AlO_x)_{0.64}(NiO)_{0.09}. NiO growth is further promoted after increasing the oxidation temperature to 500 °C and the composition of the oxide film changes to (Al₂O₃)_{0.14}(AlO_x)_{0.43}(NiO)_{0.43}. Annealing the H₂O-formed oxide film promotes the formation of Al₂O₃ by consuming the defective AlO_x and NiO, and the composition of the oxide film changes to (Al₂O₃)_{0.23}(AlO_x)_{0.42}(NiO)_{0.35} after the vacuum annealing at 500 °C and then to (Al₂O₃)_{0.71}(AlO_x)_{0.22}(NiO)_{0.07} after further annealing at 750 °C. The composition evolution of the oxide overlayer can be monitored *in situ* at elevated temperature and pressure with the AP-XPS as shown above. Such important information cannot be readily obtained with the use of a UHV-based XPS system (typically at pressures < 10⁻⁵ Torr) or

exposure at high pressure in a separate chamber followed by transfer to UHV for analysis because the sample transfers can interrupt the reaction and induce oxide decomposition (e.g., NiO) or change the composition (e.g., AlO_x) of the oxide overlayer.

4. Discussion

The detailed comparison of the oxidation of the NiAl(100) surface by O_2 and H_2O described above illustrates that the O_2 -formed oxide films have a more stoichiometric composition than the H_2O -formed oxide films under the same conditions of pressure and temperature. The different oxide film compositions have direct consequence on the passivation properties of the oxide films. As shown in Figs. 6, no NiO formation occurs for O_2 exposure at any temperatures. In contrast, H_2O exposure results in NiO growth at 300 °C, and further increasing the oxidation temperature leads to significant NiO growth, for which the fraction of NiO in the oxide film increases from 9% at 300 °C to 43% at 500 °C.

The experimental results presented above reveal that the NiAl alloy exhibits selective oxidation during O_2 oxidation, in which only Al participates in the oxide film formation (Figs. 1, 6). In contrast, H_2O oxidation at $T > 300$ °C results in the simultaneous NiO growth (Figs. 4, 6). From a thermodynamic point of view, the formation of aluminum oxide is energetically strongly favored over the NiO formation. The selective oxidation of Al in the NiAl alloy results in the enrichment of Ni in the oxide/substrate interface region, which has been observed for the oxidation of the NiAl(100) under UHV conditions.^{12, 13} In view of the much higher gas pressure in the present work, significant Ni enrichment can occur in the subsurface region because of the growth of the much thicker aluminum oxide film compared to the oxidation under the UHV conditions. As shown in Figs. 1 and 4, the O_2 -formed aluminum oxide film is dominated by stoichiometric Al_2O_3 , which is more compact compared to the H_2O -formed oxide film that is dominated by defective AlO_x . Therefore, the O_2 -formed aluminum oxide film is a more effective barrier than the H_2O -formed oxide film in blocking the outward diffusion of Ni atoms from the subsurface region.

The equilibrium oxygen pressure for selective oxidation of one component of an alloy depends on the alloy composition. The significant enrichment of Ni underneath the aluminum oxide layer lowers the equilibrium oxygen pressure for Ni oxidation. Therefore, Ni can be driven to the outer surface through the existing aluminum oxide layer to form NiO if allowed kinetically. As shown above, the O₂-formed oxide film is dominated by the stoichiometric Al₂O₃, for which the dense and compact atomic structure of the oxide film can provide better protection to the metallic substrate by barring the outward diffusion of the Ni. Therefore, NiO formation is kinetically prohibited even at the elevated temperature of 500 °C, as shown in Fig. 1. In contrast, the composition of the H₂O-formed oxide film is dominated by defective AlO_x, for which the outward diffusion of Ni can be significantly promoted from the Ni-rich region underneath the aluminum oxide overlayer. As shown in Fig. 6, a critical temperature of 300 °C is required to activate the outward diffusion of Ni through the defective aluminum oxide layer. The outward diffusion of Ni is further promoted after increasing the oxidation temperature to 500 °C, which results in significantly more NiO growth (Fig. 6).

5. CONCLUSIONS

A comparative study of the oxidation of NiAl(100) by molecular oxygen and water vapor at a near-ambient pressure (0.2 Torr) is performed with ambient pressure X-ray photoelectron spectroscopy. O₂ exposure leads to the selective oxidation of Al at temperatures ranging from 40 °C to 500 °C. In contrast, H₂O exposure results in the selective oxidation of Al at 40 °C and 200 °C; increasing the oxidation temperature above 300 °C leads to the simultaneous NiO formation. Based on the detailed analyses of the binding energy shift and the evolution of the relative intensity of O 1s, Al³⁺ 2p, and Ni 3p peaks, we show that the oxide film formed from O₂ oxidation has a stoichiometric Al₂O₃ structure that provides improved protection to the metallic substrate by barring the outward diffusion of the Ni. In contrast, the aluminum oxide film formed by H₂O oxidation has a defective (and thus less protective) structure that

allows outward diffusion of Ni for simultaneous NiO formation. These results demonstrate that the passivation properties of an oxide film depend on the type of the oxidizing species used for the surface passivation.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0001135. Research carried out in part at the Center for Functional Nanomaterials and National Synchrotron Light Source, which are supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

REFERENCES:

1. Lin, W.-C.; Kuo, C.-C.; Luo, M.-F.; Song, K.-J.; Lin, M.-T., Self-aligned Co nanoparticle chains supported by single-crystalline $\text{Al}_2\text{O}_3/\text{NiAl}(100)$ template. *Applied Physics Letters* **2005**, 86, (4), 043105.
2. Luo, M. F.; Chiang, C. I.; Shiu, H. W.; Sartale, S. D.; Kuo, C. C., Patterning Co nanoclusters on thin-film $\text{Al}_2\text{O}_3/\text{NiAl}(100)$. *Nanotechnology* **2006**, 17, (2), 360.
3. Sartale, S. D.; Shiu, H. W.; Ten, M. H.; Huang, J. Y.; Luo, M. F., Scanning tunneling microscopy study of growth of Pt nanoclusters on thin film $\text{Al}_2\text{O}_3/\text{NiAl}(100)$. *Surface Science* **2006**, 600, (22), 4978-4985.
4. Luo, M. F.; Shiu, H. W.; Ten, M. H.; Sartale, S. D.; Chiang, C. I.; Lin, Y. C.; Hsu, Y. J., Growth and electronic properties of Au nanoclusters on thin-film $\text{Al}_2\text{O}_3/\text{NiAl}(100)$ studied by scanning tunnelling microscopy and photoelectron spectroscopy with synchrotron radiation. *Surface Science* **2008**, 602, (1), 241-248.
5. Méndez, J.; Niehus, H., Growth of chromium on the structured surface of $\text{Al}_2\text{O}_3/\text{NiAl}(100)$. *Applied Surface Science* **1999**, 142, (1-4), 152-158.
6. Gaßmann, P.; Franchy, R.; Ibach, H., Preparation of a well ordered aluminum oxide layer on $\text{NiAl}(001)$. *Journal of Electron Spectroscopy and Related Phenomena* **1993**, 64, 315-320.
7. Gassmann, P.; Franchy, R.; Ibach, H., Investigations on phase transitions within thin Al_2O_3 layers on $\text{NiAl}(001)$ — HREELS on aluminum oxide films. *Surface Science* **1994**, 319, (1), 95-109.
8. Blum, R.-P.; Ahlbehrendt, D.; Niehus, H., Growth of Al_2O_3 stripes in $\text{NiAl}(001)$. *Surface Science* **1998**, 396, (1), 176-188.
9. Qin, H.; Zhou, G., The formation of double-row oxide stripes during the initial oxidation of $\text{NiAl}(100)$. *Journal of Applied Physics* **2013**, 114, (8), 083513.
10. Qin, H.; Sutter, P.; Zhou, G., The Crystallization of Amorphous Aluminum Oxide Thin Films Grown on $\text{NiAl}(100)$. *Journal of the American Ceramic Society* **2014**, 97, (9), 2762-2769.
11. Frémy, N.; Maurice, V.; Marcus, P., X-ray photoelectron spectroscopy study of thin oxide layers formed on (001)-oriented β - NiAl single-crystal surfaces. *Surface and Interface Analysis* **2002**, 34, (1), 519-523.
12. Cai, N.; Liu, Q.; Tong, X.; Zhou, G., X-ray Photoelectron Spectroscopy Study of the Passivation of $\text{NiAl}(100)$ by Water Vapor. *Langmuir* **2014**, 30, (3), 774-783.
13. Cai, N.; Qin, H.; Tong, X.; Zhou, G., Growth of ultrathin amorphous alumina films during the oxidation of $\text{NiAl}(100)$. *Surface Science* **2013**, 618, 20-26.
14. Blum, R.-P.; Niehus, H., Initial growth of Al_2O_3 on $\text{NiAl}(001)$. *Applied Physics A* **1998**, 66, (1), S529-S533.
15. Frémy, N.; Maurice, V.; Marcus, P., Initial Stages of Growth of Alumina on $\text{NiAl}(001)$ at 1025 K. *Journal of the American Ceramic Society* **2003**, 86, (4), 669-75.
16. Qin, H.; Chen, X.; Li, L.; Sutter, P. W.; Zhou, G., Oxidation-driven surface dynamics on $\text{NiAl}(100)$. *Proceedings of the National Academy of Sciences* **2015**, 112, (2), E103-E109.
17. Toyoshima, R.; Shimura, M.; Yoshida, M.; Monya, Y.; Suzuki, K.; Amemiya, K.; Mase, K.; Mun, B. S.; Kondoh, H., A near-ambient-pressure XPS study on catalytic CO oxidation reaction over a $\text{Ru}(1010)$ surface. *Surface Science* **2014**, 621, 128-132.
18. Eren, B.; Heine, C.; Bluhm, H.; Somorjai, G. A.; Salmeron, M., Catalyst Chemical State during CO Oxidation Reaction on $\text{Cu}(111)$ Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy and Near Edge X-ray Adsorption Fine Structure Spectroscopy. *Journal of the American Chemical Society* **2015**, 137, (34), 11186-11190.
19. Lee, H. C.; Kim, B. M.; Jeong, C. K.; Toyoshima, R.; Kondoh, H.; Shimada, T.; Mase, K.; Mao, B.; Liu, Z.; Lee, H.; Huang, C.-Q.; Li, W. X.; Ross, P. N.; Mun, B. S., Surface segregation and oxidation of $\text{Pt}_3\text{Ni}(111)$ alloys under oxygen environment. *Catalysis Today* **2016**, 260, 3-7.

20. Shavorskiy, A.; Müller, K.; Newberg, J. T.; Starr, D. E.; Bluhm, H., Hydroxylation of Ultrathin $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ Films at Environmental Humidity. *The Journal of Physical Chemistry C* **2014**, 118, (50), 29340-29349.
21. Starr, D. E.; Liu, Z.; Havecker, M.; Knop-Gericke, A.; Bluhm, H., Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy. *Chemical Society Reviews* **2013**, 42, (13), 5833-5857.
22. Maurice, V.; Frémy, N.; Marcus, P., Hydroxylation-induced modifications of the $\text{Al}_2\text{O}_3/\text{NiAl}(001)$ surface at low water vapour pressure. *Surface Science* **2005**, 581, (1), 88-104.
23. Marcus, P.; Hinnen, C.; Olefjord, I., Determination of attenuation lengths of photoelectrons in aluminium and aluminium oxide by angle-dependent x-ray photoelectron spectroscopy. *Surface and Interface Analysis* **1993**, 20, (11), 923-929.
24. Delgass, W. N.; Hall, G. L.; Kellerman, R.; Lunsford, J. H., Spectroscopy in Heterogeneous Catalysis, Academic press, New York. **1979**.
25. Jeurgens, L. P. H.; Sloof, W. G.; Tichelaar, F. D.; Mittemeijer, E. J., Composition and chemical state of the ions of aluminium-oxide films formed by thermal oxidation of aluminium. *Surface Science* **2002**, 506, (3), 313-332.
26. Chen, C.; Splinter, S. J.; Do, T.; McIntyre, N. S., Measurement of oxide film growth on Mg and Al surfaces over extended periods using XPS. *Surface Science* **1997**, 382, (1), L652-L657.
27. Garza, M.; Magtoto, N. P.; Kelber, J. A., Characterization of oxidized $\text{Ni}_3\text{Al}(110)$ and interaction of the oxide film with water vapor. *Surface Science* **2002**, 519, (3), 259-268.
28. Cai, N.; Zhou, G.; Müller, K.; Starr, D. E., Tuning the Limiting Thickness of a Thin Oxide Layer on $\text{Al}(111)$ with Oxygen Gas Pressure. *Physical Review Letters* **2011**, 107, (3), 035502.
29. Venezia, A. M.; Loxton, C. M., Low pressure oxidation of Ni_3Al alloys at elevated temperatures as studied by x-ray photoelectron spectroscopy and Auger spectroscopy. *Surface Science* **1988**, 194, (1), 136-148.
30. Bianconi, A.; Bachrach, R. Z.; Hagstrom, S. B. M.; Flodström, S. A., Al- Al_2O_3 interface study using surface soft-x-ray absorption and photoemission spectroscopy. *Physical Review B* **1979**, 19, (6), 2837-2843.
31. Graupner, H.; Hammer, L.; Heinz, K.; Zehner, D. M., Oxidation of low-index FeAl surfaces. *Surface Science* **1997**, 380, (2), 335-351.
32. Niu, C.; Shepherd, K.; Martini, D.; Tong, J.; Kelber, J. A.; Jennison, D. R.; Bogicevic, A., Cu interactions with $\alpha\text{-Al}_2\text{O}_3(0001)$: effects of surface hydroxyl groups versus dehydroxylation by Ar-ion sputtering. *Surface Science* **2000**, 465, (1-2), 163-176.
33. Cai, N.; Zhou, G.; Müller, K.; Starr, D. E., Comparative Study of the Passivation of $\text{Al}(111)$ by Molecular Oxygen and Water Vapor. *The Journal of Physical Chemistry C* **2013**, 117, (1), 172-178.
34. Digne, M.; Sautet, P.; Raybaud, P.; Toulhoat, H.; Artacho, E., Structure and Stability of Aluminum Hydroxides: A Theoretical Study. *The Journal of Physical Chemistry B* **2002**, 106, (20), 5155-5162.
35. Calow, C. A.; Porter, I. T., The solid state bonding of nickel to alumina. *Journal of Materials Science* **1971**, 6, (2), 156-163.
36. Loginova, E.; Cosandey, F.; Madey, T. E., Nanoscopic nickel aluminate spinel (NiAl_2O_4) formation during $\text{NiAl}(111)$ oxidation. *Surface Science* **2007**, 601, (3), L11-L14.
37. Cappus, D.; Xu, C.; Ehrlich, D.; Dillmann, B.; Ventrice, C. A.; Al Shamery, K.; Kuhlenbeck, H.; Freund, H. J., Hydroxyl groups on oxide surfaces: $\text{NiO}(100)$, $\text{NiO}(111)$ and $\text{Cr}_2\text{O}_3(111)$. *Chemical Physics* **1993**, 177, (2), 533-546.
38. Tyuliev, G. T.; Kostov, K. L., XPS/HREELS study of NiO films grown on $\text{Ni}(111)$. *Physical Review B* **1999**, 60, (4), 2900-2907.
39. Sobczak, N.; Oblakowski, J.; Nowak, R.; Kudyba, A.; Radziwill, W., Interaction between liquid aluminum and NiO single crystals. *Journal of Materials Science* **2005**, 40, (9), 2313-2318.

40. Wen, J. Z.; Ringuette, S.; Bohlouli-Zanjani, G.; Hu, A.; Nguyen, N. H.; Persic, J.; Petre, C. F.; Zhou, Y. N., Characterization of thermochemical properties of Al nanoparticle and NiO nanowire composites. *Nanoscale Research Letters* **2013**, 8, (1), 1-9.
41. Becker, C.; Kandler, J.; Raaf, H.; Linke, R.; Pelster, T.; Dräger, M.; Tanemura, M.; Wandelt, K., Oxygen adsorption and oxide formation on Ni₃Al (111). *Journal of Vacuum Science & Technology A* **1998**, 16, (3), 1000-1005.

Table 1: Conditions for the O₂ and H₂O oxidation of NiAl(100) and subsequent annealing of the oxide film

Temperature (°C)	40	200	300	500	500 vacuum annealing	750 vacuum annealing
O₂	30 min	30 min	30 min	30 min	30 min	30 min
H₂O	25 min	20 min	30 min	40 min	20 min	20 min

Table 2: Comparisons of binding energies of O 1s of the O₂- and H₂O-formed oxide films

	O 1s									
	AlO _x		Amorphous Al ₂ O ₃		γ -Al ₂ O ₃		Al-OH		NiO	
	O ₂ (eV)	H ₂ O (eV)	O ₂ (eV)	H ₂ O (eV)	O ₂ (eV)	H ₂ O (eV)	O ₂ (eV)	H ₂ O (eV)	O ₂ (eV)	H ₂ O (eV)
40 °C	531.3	531.3	532.4	532.4	--	--	--	533.8	--	--
200 °C	--	531.3	532.4	532.4	--	--	--	533.8	--	--
300 °C	--	531.3	532.4	532.4	533.3	--	--	--	--	530.3
500 °C	--	531.3	532.4	532.4	533.3	--	--	--	--	530.3
500 °C vacuum Annealing	--	531.3	532.4	532.4	533.3	--	--	--	--	530.3
750 °C vacuum Annealing	--	531.3	532.4	532.4	533.3	533.3	--	--	--	530.3

Table 3: Thicknesses of the aluminum oxide films for the O₂ and H₂O oxidation of NiAl(100) and subsequent vacuum annealing

Temperature (°C)	40	200	300	500	500 Annealing	750 Annealing
O ₂	10.8 Å	16.3 Å	22.0 Å	--	--	--
H ₂ O	6.1 Å	15.7 Å	--	--	--	--

Figure captions:

Figure 1: Photoemission spectra of the O 1s (a) and Al 2p - Ni 3p (b) regions of the NiAl(100) during the stepwise O₂ oxidation at $p(\text{O}_2) = 0.2$ Torr and $T = 40, 200, 300,$ and 500 °C, respectively. Oxidation time is 30 min at each T .

Figure 2: Photoemission spectra of the (a) O 1s and (b) Al 2p – Ni 3p regions of the NiAl(100) during the stepwise O₂ oxidation at $p(\text{O}_2) = 0.2$ Torr, and subsequent annealing at 500 °C and then at 750 °C for 30 min each. The spectra for vacuum annealing were taken in vacuum at corresponding annealing temperatures.

Figure 3: Evolution of the binding energies of O 1s (a) and Al^{3+} 2p (b) during O_2 oxidation at $p(O_2) = 0.2$ Torr with stepwise temperature increase from $T = 40$ $^{\circ}C$ to 500 $^{\circ}C$ followed by vacuum annealing at 500 $^{\circ}C$ and then at 700 $^{\circ}C$ as shown in Figs. 1 and 2.

Figure 4: Photoemission spectra of the O 1s (a) and Al 2p - Ni 3p (b) regions of the NiAl(100) during the stepwise H₂O oxidation at $p(\text{H}_2\text{O}) = 0.2$ Torr and $T = 40, 200, 300,$ and 500 °C, respectively. Oxidation time is 25 min, 20 min, 30 min, and 40 min, respectively, at each T .

Figure 5: Photoemission spectra of the (a) O 1s and (b) Al 2p – Ni 3p regions of the NiAl(100) during the stepwise H_2O oxidation at $p(\text{H}_2\text{O}) = 0.2$ Torr, and subsequent vacuum annealing at 500 °C and then 750 °C for 30 min each.

Figure 6: Temperature dependence of the composition of the oxide film, (a) O_2 oxidation, (b) H_2O oxidation.

Table of content graphic