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The effect of Pt on Ni₃Al surface oxidation at low-pressures

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Abstract

The fully-oxidized surface that forms on (111) oriented Ni₃Al single crystals, with and without Pt addition, at 300–900 K under oxygen pressures of ca. 10^{-7} Torr was studied using XPS, AES, and LEIS. Two main types of surfaces form, depending upon oxidation temperature. At low-temperature, the predominant oxide is NiO, capped by a thin layer of aluminum oxide, which we refer to generically as Al_xO_y. At high-temperature (i.e., 700–800 K), NiO is replaced by a thick layer of Al_xO_y. By comparing samples that contain 0, 10 and 20 at.% Pt in the bulk, we find that the effect of Pt is to: (1) reduce the maximum amount of both NiO and Al_xO_y; and (2) shift the establishment of the thick Al_xO_y layer to lower temperatures. Platinum also decreases the adsorption probability of oxygen on the clean surface.

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1. Introduction

Certain properties of the intermetallic alloy Ni₃Al, such as high-strength at elevated temperatures and low-density, make it an attractive constituent phase in materials used for high-temperature components in turbine engines [1– 3]. High-temperature oxidation of Ni₃Al at atmospheric pressure typically leads to the formation of a complex group of oxides, including Al₂O₃, NiO, and NiAl₂O₄ [4– 6]. Recent studies have shown that adding Pt to Ni₃Al can significantly improve its oxidation resistance at elevated temperatures by promoting the preferential formation of an adherent, Al₂O₃-rich scale [7,8]. It has been suggested that the effect of Pt is, at least in part, to kinetically favor the formation of aluminum oxide by decreasing the nickel available for oxidation. This is attributable to the preferential substitution of Pt at Ni sites in the ordered $L1_2$ crystal structure of Ni₃Al [9]. In other words, the addition of Pt increases the Al/Ni ratio at the Ni₃Al surface.

The structure and composition of the oxide formed during the *initial* stages of oxidation are thought to be an important factor in determining the resistance of Ni–Al alloys to corrosion and spallation [10,11]. Ultrahigh vacuum (UHV) conditions can probe this regime very well because of the low-oxygen pressure (low-flux) at which oxidation is carried out—typically in the range of 10^{-8} to 10^{-5} Torr.

There have been numerous oxidation studies on both Ni₃Al and NiAl at low-pressures. Some useful generalizations can be drawn from those studies. *First*, it is well-established that an amorphous layer of alumina (with short-range order) develops when the sample is oxidized at low-temperatures. A crystalline Al₂O₃ layer develops when the sample is oxidized at high-temperatures. For Ni₃Al(111), this 5–7 Å crystalline layer has been identified as γ -like Al₂O₃ [12–14]. For both alloys, the transition occurs around 700–800 K [10,11]. It has been proposed that this transition marks the onset of long-range diffusion

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of Al between the bulk and surface, on the time scale of oxidation [15,16].

Two other chemical species have also been identified. At room temperature, the oxide is preceded by chemisorbed oxygen at low-coverage, distinguishable from the oxide by its adsorption kinetics. In addition, an aluminum oxide with Al in an oxidation state lower than that in Al₂O₃ exists on Ni₃Al surfaces. Several possible explanations have been given for this state [17–20].

Second, aluminum oxide is favored thermodynamically over the Ni-containing oxides, NiO and NiAl₂O₄, but the latter are faster-growing and hence favored kinetically [12,20]. One of the nickel-containing oxides, NiAl₂O₄, is not known to form on either Ni₃Al or NiAl at low-pressures [10,12,16,17,21]. On NiAl surfaces, NiO has not been observed at any temperature; however, on Ni₃Al surfaces, NiO has been observed by some authors, in addition to the alumina layer described above [14,17,22]. Presumably, NiO forms on Ni₃Al but not on NiAl because the former has a higher Ni concentration.

Despite these previous works, the chemical nature of oxide formed upon saturation and how it changes with oxidation temperature have not been systematically examined. In this work, our goal was to systematically probe the amount, chemical nature, and spatial distribution of the oxide that forms upon saturation at an oxygen pressure of about 10^{-7} Torr, as a function of oxidation temperature. In this way, we hoped to gain insight into the initial stages of the formation of the protective phase. Information is derived from X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and Auger electron spectroscopy (AES). We are particularly interested in the effect of Pt, and therefore we compare samples of (111) oriented Ni₃Al single crystals with and without Pt addition.

2. Experimental description

The methods of sample preparation and characterization were the same as described elsewhere [23]. XPS and LEIS were performed in one chamber, while AES was carried out in a separate chamber, on parallel sets of samples. XPS and LEIS measurements were performed by means of a hemispherical analyzer with multi-channel detector. For XPS, the incident X-rays were monochromatized Al Ka (hv = 1486.6 eV) radiation operated at 15 kV and 250 W. The XPS instrument was a Perkin Elmer PHI 5500, multi-technique system, fitted with an Omni Focus III lens system and run with PHI-Access software. The XPS energy scale was calibrated using Au4 $f_{7/2}$ and Cu2 $p_{3/2}$ at 84.0 eV and 932.6 eV, respectively. The energy resolution was 0.65 eV at pass energy of 58.7 eV, judging from Ag $3d_{5/2}$ photoelectrons. For LEIS we used a beam of He⁺ at 1 keV and at a current of approximately 3×10^{-8} A/cm². Data were acquired in two modes, fixed and variable angle. In the fixed mode, the emission angle was 45°. In the variable angle mode, the emission angle varied from 15 to 70°. The Auger beam energy is 5 keV.

The Auger beam current is $1.8 \,\mu A$ from sample to ground without bias.

The single-crystal samples were prepared by the Materials Preparation Center at the Ames Laboratory [24]. Based upon electron probe microanalysis (EPMA) of different areas on each sample, the compositions of the samples used for XPS and LEIS were $Pt_0Ni_{77.4\pm0.3}Al_{22.6\pm0.3}$ (hereafter called the 0%-Pt sample), $Pt_{9.7\pm0.1}Ni_{65.3\pm0.3}Al_{25.0\pm0.3}$ (called 10%-Pt), and $Pt_{20.4\pm0.1}Ni_{54.7\pm0.2}Al_{24.9\pm0.2}$ (called 20%-Pt). The compositions, and standard deviations in composition, were similar for the samples used in AES– LEED. The standard deviations quoted above reflect small and nonsystematic spatial variations in composition, which in turn indicate good spatial homogeneity.

Pressures in the chamber were measured by a vendorcalibrated nude ion. Exposures are reported in terms of Langmuir (1 L = 10^{-6} Torr s) and have not been corrected for ion gauge sensitivities (relative to N₂, the calibration gas) or flux to the sample. The oxidation conditions were as follows. In the AES-LEED chamber, oxygen was introduced by backfilling the chamber to a constant pressure of 2×10^{-7} Torr. An exposure of about 1000 L corresponded to saturation at this pressure. In the XPS-LEIS chamber, oxygen was introduced through a tube that was 1 mm in internal diameter and about 2 mm from the sample. Comparison of the oxygen uptake curves from XPS and AES suggested that the local oxygen pressure at the sample in the XPS-LEIS chamber was also in the low 10^{-7} Torr range. Spectra were recorded after evacuating the chamber. On the time scale of our experiments, the spectra remained invariant after evacuation.

In the XPS data, overlap between lines of Pt, Ni, and Al prevented use of certain peaks that are considered standards. In particular, the Al2p could not be used because it overlapped completely with the $Pt4f_{5/2}$, and both were close to the Ni3p. These issues led us to choose the Al2s,



Fig. 1. XPS spectra of 0%-Pt Ni₃Al(111), clean and after oxidation to saturation at various temperatures.

Ni2p_{3/2}, and Pt4d_{5/2} from among the metal peaks. The first two are shown in Figs. 1–3. Experimental spectra were analyzed by fitting to component peaks using PHI's MultiPak software. The binding energies and full width at half maxima (FWHM) were kept constant for a given elemental or oxidic peak throughout the fitting of all experimental data.

In XPS, the composition of the oxide film was calculated from the intensities (peak areas) of O1s, $Ni2p_{3/2}$, Al2s and Pt4d_{5/2} spectra using the following relationship [25]:

$$X_{\mathbf{A}} = \frac{I_{\mathbf{A}}/I_{\mathbf{A}}^{\infty}}{\sum_{i=\mathcal{A},\mathcal{B}} I_i/I_i^{\infty}},\tag{1}$$

where X_A , I_A and I_A^{∞} , respectively, represents the atomic concentration, XPS intensity and published atomic sensi-



Fig. 2. XPS spectra of 10%-Pt Ni₃Al(111), clean and after oxidation to saturation at various temperatures.



Fig. 3. XPS spectra of 20%-Pt $Ni_3Al(111)$, clean and after oxidation to saturation at various temperatures.

tivity factor [26] appropriate to the spectrometer for element A. The sum is over all of the constituents of the solid. In AES, intensities were determined from peak-topeak height and published atomic sensitivity factors [27] were employed in quantification.

For the LEIS results reported here, the incident beam impinged on the surface at an angle of 40° with respect to the surface normal. The scattering angle was 135°. In order to calculate relative atomic concentrations, the differential scattering cross-section for each element, given our scattering conditions, was calculated using the ZBL screened Coulomb potential [28]. The broad background arising from inelastic processes and subsurface scattering was removed prior to determining the peak areas.

3. Experimental results and interpretation

Figs. 1–3 show a series of XPS spectra obtained on the three different samples. Fig. 1 represents the 0%-Pt sample, Fig. 2 the 10%-Pt sample, and Fig. 3 the 20%-Pt sample. The bottom spectrum represents the clean alloy, while higher spectra show the result of oxidizing to saturation. The temperature of oxidation increases, going upward, from room temperature to 900 K. For each sample and each temperature, three photoemission peaks are shown: Al2s, O1s, and Ni2p. For the Pt-containing samples, the Pt4d_{5/2} peak was also examined, but is not shown. It exhibits no evidence of oxidation.

Both the Ni2p and Al2s peaks indicate oxidation of the Ni and Al, because the metal peaks broaden toward higher binding energy, sometimes leading to a discernible peak, in going from the bottom spectrum upward. For Al2s, the oxide peak is usually clear, as can be seen in Figs. 1-3. For Ni2p, the oxide (Ni²⁺) intensity is always relatively small, nestled between the metallic Ni2p_{3/2} peak (853.2 eV) and its satellite peak (858.6 eV). The Ni^{2+} line is expected to be a doublet for NiO at 854.1 and 855.9 eV [29] and a single peak for NiAl₂O₄ at 857 eV [6,30]. The best fit using a single peak led to a peak energy of 855.5 eV, in disagreement with the position expected for NiAl₂O₄. The fit was significantly better with a doublet at the positions expected for NiO. (Fits also allowed different relative intensities of satellite peaks for the oxide and the metal.) Analysis of XPS peak intensities, below, further rules out the presence of the spinel phase.

The O1s spectra in Figs. 1–3 are fitted well with three components having FWHM of 1.9 eV at 530.3 eV (NiO [17,31–33]), 531.4 eV, and 532.2 eV (Al₂O₃ [17,34,35]). The oxygen component at 531.4 eV could have multiple assignments. It could be oxygen associated purely with the nickel. For instance, other authors have assigned a peak at about this binding energy to Ni₂O₃ or to "defect" nickel oxide on surfaces of pure Ni [36,37]. Alternatively, it could be oxygen associated both with nickel and aluminum, perhaps in the spinel phase, NiAl₂O₄. Third, it could be associated only with the aluminum in a form that is commonly designated AlO_x (i.e., a type of aluminum oxide

with an aluminum oxidation state intermediate between Al_2O_3 and Al metal) [11,16,17,20,38]. To distinguish between these possibilities, we checked whether the intensities of the (weak) Ni²⁺ peaks in the Ni2p region were correlated with the intensity of the O1s peak at 531.4 eV, as a function of oxidation temperature. The result is shown in Fig. 4 for 0%-Pt, the alloy where the Ni²⁺ peaks are strongest. The trend is similar in the other two alloys. The anti-correlation between the intensities of Ni²⁺, and O1s at 531.4 eV, clearly rules out a form of the oxide associated with nickel, such as Ni₂O₃ or spinel, in agreement with conclusions by other authors for this alloy [17]. Therefore, the O1s line at 531.4 eV is assigned to AlO_x.

In the remainder of this paper, we focus on the total nickel oxide and aluminum oxide concentrations from the O1s data. Since both Al_2O_3 and AlO_x are aluminum oxides, the sum of their contribution (which we denote as " Al_xO_y ") is employed. All of the trends are reproduced



Fig. 4. Compositions of the Ni2p_{3/2} doublet in XPS at 854.1 eV and 855.9 eV, and of the O1s peak at 531.4 eV, at saturation, as a function of temperature for the 0%-Pt sample. The *y*-axis shows the concentrations of the species associated with these features, based on their intensities.

qualitatively if the Al2s and Ni2p oxidic lines are used instead of the O1s components.

Fig. 5(a) shows the total oxygen concentration at saturation as a function of oxidation temperature, measured with XPS. The curves are depressed for higher Pt content, meaning that higher Pt content leads to less oxygen incorporation. This is true at all temperatures except 700 K. Furthermore, Pt changes the shapes of the curves. For 0%-Pt, the curve shows two maxima, at around 500 and 800 K. For 10%-Pt and 20%-Pt, there is only one maximum, at around 700 K. The AES data for the two Pt-containing alloys, shown in Fig. 5(b), are complementary and confirm certain trends in the data. One is the presence of a single maximum in total oxygen concentration at 700 K for both of the Pt-containing samples. Another is the fact that oxygen concentration is lower for 20%-Pt than for 10%-Pt.

The variation in total oxygen concentration is broken down into contributions from NiO and Al_xO_y , based on the O1s spectra, in Fig. 6(a)-(c). In Fig. 6(a), this deconvolution shows that the maxima in the total oxygen concentration for the 0%-Pt sample are due, first, to a peak at 500 K in the NiO concentration, and second, to a peak at 800 K in the $Al_x O_y$ concentration. In each case, the variation in concentration of the other oxide is small around the maximum, so the peak in total content is due to the variation of a single constituent. Fig. 6(b) and (c) show that one effect of Pt is to shift the rise in Al_xO_y concentration to lower temperatures, so that the sum of the two curves gives a single maximum at 700 K. The rise in Al_xO_y concentration begins at about 700 K in the absence of Pt, and at about 500 K in the presence of Pt. Hence, the presence of Pt shifts the increase in Al oxidation downward by about 200 K. This shift is not progressive with Pt concentration, but rather is constant for both the 10%-Pt and 20%-Pt samples. Pt also reduces the maximum amount of NiO, from 34 at.% to 25 at.% to 18 at.%, in going from Fig. 6(a) to (b) to (c). This reduction is not balanced by an equal gain in $Al_x O_y$, so the net effect is to decrease the total oxygen content at 500 K (Fig. 5). Pt also reduces the maximum concentration



Fig. 5. Oxygen composition at saturation, as a function of temperature. (a) XPS data (using O1s spectra); (b) AES data (using O KLL line). For XPS, all points represent experiments that were repeated 2 or 3 times except 300 K for 0%-Pt sample and 500 and 800 K for 10%-Pt and 20%-Pt samples. In some cases, error bars are so small that they are obscured by the symbol. For AES, there was only 1 run for all points.



Fig. 6. Concentrations of oxygen, NiO and Al_xO_y at saturation: (a) 0%-Pt; (b) 10%-Pt; (c) 20%-Pt. All data are based on the O1s line in XPS. NiO and Al_xO_y concentrations were calculated by deconvoluting the O1s spectra as described in the text.

of Al_xO_y produced at higher temperatures, for instance from 45 at.% at 800 K in Fig. 6(a), to 23 at.% at 800 K in Fig. 6(b). In summary, Pt reduces the extent of oxidation of both Ni and Al.

These observations serve to explain the trends in Fig. 5. The total oxygen uptake is suppressed by Pt because the extents Ni and Al oxidation are reduced by Pt. At 700 K, the uptake curves for the two Pt-containing samples cross-over the curve for the 0%-Pt alloy simply because the maximum in the amount of Al_xO_y formation is shifted to lower temperature by Pt.

There is evidence that aluminum oxide is always the principal constituent in the topmost surface layer, even when nickel forms the predominant oxide. This is demonstrated by the angle-resolved XPS data of Fig. 7, and by the LEIS data of Fig. 8. In Fig. 7, a higher value of the



Fig. 7. XPS angle resolved data after saturation oxidation of 10%-Pt Ni₃Al(111) at 300 K. The concentrations of each species are normalized to the value at 70° , which is the signal with the highest bulk contribution. (a) Total elemental concentration ratios. (b) Oxide concentration ratios from the O1s data.

take-off angle corresponds to a lower contribution of the surface signal to the total signal. Fig. 7(a) shows the total signal originating from each of four elements-Ni, Pt, Al, and O-as a function of angle. For each element, the angle-resolved data are normalized to the value at 70°, which is the value closest to the bulk limit. For the 10%-Pt sample oxidized at 300 K, the Al and O signals are above one, while the Ni and Pt signals are below one, at low-angles. This means that the surface is enriched in Al and O, and depleted in Pt and Ni, relative to bulk concentrations. Yet, Fig. 6(b) also shows that the oxide is mainly NiO at 300 K, suggesting that even at room temperature, the kinetics of Al oxidation are sufficiently fast to form a thin surface layer of $Al_x O_y$. Qualitatively, the trends shown in Fig. 7(a) are robust. For all samples and all temperatures, the normalized total Al2s and O1s intensities exceed one at low-angles, while the Ni2p_{3/2} and Pt4d_{5/2} (if present) are below one at low-angles. This means that Al_xO_y is always the principal constituent in the outermost layer, even under conditions where it is not the predominant oxide, and regardless of whether Pt is present.

These conclusions are strengthened by the XPS data of Fig. 7(b), which show the angular variation of the O1s signals originating separately from NiO and Al_xO_y , deconvoluted as described for Figs. 1–3, and normalized to their values at 70°. Again, the deviations from one at low-angle indicate that Al_xO_y is on top, while the NiO lies deeper. However, it is not clear from these data whether the NiO beneath the Al_xO_y is "pure" or is intermixed with metal. The qualitative trends shown in Fig. 7(b) are observed for all samples and all temperatures.

Fig. 8 shows the surface atomic concentrations derived from LEIS as a function of oxidation temperature, for 10%-Pt. (The data are similar for 20%-Pt.) Among the three metals, Al is by far the most abundant at all temperatures. For instance, at 300 K, the ratio of Al:Ni is about 3.5. By contrast, in the bulk sample this ratio is 0.4, and for the clean surface it is 0.7 from LEIS [23], showing that oxidation strongly enhances the surface concentration of



Fig. 8. LEIS data after saturation oxidation of 10%-Pt Ni₃Al(111). Experimental data were reproduced as follows: 1 run at 300, 500, and 800 K, 3 runs at 700 K, and 2 runs at 900 K.

Al. Because LEIS mainly probes the top one or two atomic layers, this confirms that $Al_x O_y$ is enriched at the surface.

Returning to Fig. 7(b), the Al_xO_v portion of the O1s signal in angle-resolved XPS is always enhanced at 15°, relative to its value at 70°. However, the degree of enhancement-the ratio of the signals at 15° and 70°-is not constant. This degree of enhancement is presented in Fig. 9 as a function of oxidation temperature, for all three samples. To interpret these data, we assume that $Al_x O_y$ is confined to a region at the surface where it is separate from the other components (NiO and the metals). Then this ratio should not depend upon the total area of Al_xO_y at the surface, but rather upon the average thickness of the Al_xO_y regions, with a lower ratio corresponding to thicker regions. In Fig. 9, for 0%-Pt, the ratio is high through 700 K, but drops sharply between 700 and 800 K. This correlates with the sharp rise in Al_xO_y concentration in Fig. 6(a). For the Pt-containing samples, the ratio drops at lower temperatures, with most of the change occurring between 500 and 700 K. Again, this correlates with the temperature range where $Al_x O_v$ concentration rises in Fig. 6(b) and (c). Thus, Pt reduces the temperature at which a thicker $Al_{x}O_{y}$ layer becomes established. The curves in Fig. 9 do not turn upward again between 800 and 900 K, where the Al_xO_y layer disappears. This signals that as the oxide disappears it does not become thinner; islands shrink laterally, not vertically.

Platinum also slows the kinetics of oxygen uptake. This can be seen from Fig. 10, which displays the oxygen concentration derived from AES using the O KLL (510 eV) line intensity versus oxygen exposure at four different temperatures. The initial slope of the curve, which is proportional to the initial sticking coefficient, S_0 , is slightly but consistently lower for 20%-Pt than for 10%-Pt. The sticking coefficient, S, is the probability that an incident molecule adsorbs on the surface. The initial sticking coefficient, S_0 , is the value in the limit of zero coverage [39]. Note that



Fig. 9. Al_xO_y at an XPS take-off angle of 15° after saturation oxidation of 0%-Pt, 10%-Pt, and 20%-Pt samples. All the data points are normalized to the value at a take-off angle of 70°, which contains the highest bulk component. Contribution of Al_xO_y is calculated by deconvoluting the O1s spectra as described in the text.



Fig. 10. Oxygen composition (from AES data) as a function of exposure at (a) 300 K; (b) 500 K; (c) 700 K; (d) 900 K.

at 300 K, adsorption seems to occur in two regimes, with a break at about 30 L. This probably reflects the transition from chemisorbed oxygen to oxide, reported by other authors for surfaces of NiAl [15,40] and Ni₃Al [41]. In those reports, the transition point ranged from 5 to 15 L at room temperature. This transition is also known on surfaces of pure Al (e.g., [42–44]) and pure Ni (e.g., [45,46]).

4. Discussion

4.1. Effects of Pt

The primary goal of our study was to elucidate the effect of Pt on oxidation of Ni₃Al. We find that Pt exerts two main effects on the oxygen-saturated surface: (1) it decreases the maximum amount of both NiO and Al_xO_y ; and (2) it shifts the formation of Al_xO_y to lower temperatures. It also slows oxygen adsorption on the clean surface. Interpretation is given below.

First, Pt decreases the amount of NiO (Fig. 6). This may simply reflect the fact that Pt replaces Ni in the bulk lattice, and so reduces the amount of Ni available for oxidation [9]. There is even more replacement of Ni by Pt at the surface than in the bulk, since Pt segregates at the clean surface [23,47]. The effect of Ni concentration is clear from a comparison of the literature for NiAl and Ni₃Al surface oxidation. At the low-oxygen pressures used in UHV experiments, NiO has never been observed on the more Ni-deficient alloy, NiAl [20,40,48,49]. However, NiO has been reported by some authors on Ni₃Al at $P < 10^{-5}$ Torr and at various temperatures [14,17,22] and its presence is confirmed in this study. Also, the maximum amount of Al_xO_y is significantly lower for both the Pt-doped samples. The maximum amount of oxygen as Al_xO_y , for instance, decreases upon going from 0%-Pt to 20%-Pt (Fig. 6). The origin of this effect is unclear.

Second, Pt shifts the enhancement of Al_xO_y to lower temperatures. This is evident both in the temperature at which the surface concentration of Al_xO_y begins to rise steeply (Fig. 6), and in the temperature at which Al_xO_v thickens (Fig. 9). In the absence of Pt, oxidation of Al accelerates strongly between 700 and 800 K and the oxide thickens in this same interval. Other authors have suggested that 700-800 K is the temperature at which longrange diffusion of Al from the bulk to the surface begins, on the time-scale of low-pressure oxidation, both for NiAl and Ni₃Al [15,16]. In this context, the natural interpretation is that Pt accelerates diffusion of Al to the surface. A higher diffusion coefficient for Al in the presence of Pt has also been inferred by Gleeson et al. based on diffusion studies of NiAl at 1400 K [7,9]. Moreover, Hayashi et al. [50] conducted a systematic interdiffusion study on Pt-modified γ -Ni and γ' -Ni₃Al alloys at 1423 K and found that the main-term ternary interdiffusion coefficient for Al, \hat{D}_{AlAl}^{Ni} , is up to a factor of three greater than the corresponding binary Ni-Al interdiffusion coefficient.

Finally, Pt slows the rate of initial oxygen uptake. This could also reflect the substitution of Pt for Ni at the clean surface. Other authors have proposed that in binary Ni–Al alloys, Ni is the more active site for oxygen dissociation, serving to increase S_0 above that for pure aluminum, which is quite low. For instance, S_0 is one on Ni(111) [45] but only 0.005 on Al(111) at 300 K [42]. The initial sticking

coefficient of oxygen on Pt is structure-dependent, but is also low on the (111) surface, with values of 0.04–0.08 at 300 K [51].

4.2. Model of oxidation

Based upon the experimental data, we propose that oxidation occurs in two broad regimes as a function of oxidation temperature. In the first regime, NiO is the most abundant oxide. It is replaced by Al_xO_y in the second regime.

First, in the temperature range 300–500 K, both Ni and Al oxidize. NiO predominates, but it lies beneath a layer that is mainly Al_xO_y . It is not clear whether the NiO is pure or intermixed with metallic species. The amount of NiO consistently peaks at 500 K. This description does not depend upon whether Pt is present. Our observation of NiO after low-pressure exposure to oxygen is generally compatible with previous reports, although the wide variety of temperatures, pressures, and annealing conditions used in previous work makes an exact comparison difficult [14,17,22].

Some Al probably diffuses from underlying layers to the surface, or Ni diffuses away from it, even at 300 K. This is because the Al:Ni ratio, measured with LEIS, increases by a such a large factor $-5\times$ - after oxidation. Exchange between the surface and underlying layers may be limited to the top few layers of the alloy, perhaps in a Cabrera–Mott mechanism. This is a logarithmic growth rate mechanism, in which the driving force for the oxide formation is an electric field set up in the oxide film resulting from a contact potential difference between metal and adsorbed oxygen. This field enables the metal ions to move through the thin oxide film independent of temperature [52,53]. This is a minor modification to previous hypotheses for the binary alloy, which said that at room temperature there is mainly or exclusively lateral diffusion of Al [14,41].

Next, in going from 500 to 700 K, less and less NiO forms. The temperature at which this decline begins (500 K) does not depend on the presence of Pt, even though the oxidation of Al does, suggesting that loss of NiO is not due to competition with Al_xO_y formation. This is also suggested by the data for the 0%-Pt alloy in Fig. 6(a), which shows significant reduction in the amount of NiO between 500 and 700 K, while the amount of Al_xO_y remains approximately constant. One must then consider other mechanisms by which the amount of NiO at saturation is reduced, one being its destabilization with increasing temperature. The oxygen partial pressure (in atm) at which there is equilibrium between Ni in the alloy and NiO can be calculated as:

$$P_{\rm O_2}^* = \frac{1}{a_{\rm Ni}^2} \exp\left(\frac{2\Delta G_{\rm NiO}^\circ}{RT}\right),\tag{2}$$

where a_{Ni} is the chemical activity of Ni in the alloy and $\Delta G_{\text{NiO}}^{\circ}$ is the standard Gibbs energy of formation of NiO,

which is given as $\Delta G_{\text{NiO}}^{\circ} = -235797 + 86.195 T \text{ (J/mol)}$ [54]. Formation of NiO is thermodynamically possible only if $P_{O_2} > P_{O_2}^*$. Eq. (2) can alternatively be used to calculate the maximum temperature at which NiO is stable under a constant P_{O_2} of 3×10^{-8} Torr which reflects the current experimental conditions. In view of the lack of experimental data for a_{Ni} in the Ni-Al and Ni-Al-Pt systems at low-temperatures, we assume ideal solution behavior, i.e., $a_{Ni} = x_{Ni} = 0.75$, and calculate $T_{max} = 1253$ K. Thus, NiO should be stable, relative to gaseous oxygen and metallic nickel, at the pressures used in our experiments. The remaining possibility is that NiO dissociates and releases dissolved oxygen at temperatures above 500 K. This scenario is consistent with a careful study of the thermal decomposition of chemisorbed oxygen at the surface of Ni(110) by Holloway and Outlaw, who found that the oxygen disappeared into the bulk at about 600 K when the sample was heated in UHV [55].

The concentration of Al_xO_y remains low and constant to a certain temperature (700 K for 0%-Pt, 500 K for 10%-Pt and 20%-Pt), then rises; simultaneously, it thickens. This is the second main regime. As discussed above, we believe that the rise in Al_xO_y reflects the onset of long-range diffusion of Al from the bulk, on the time scale of oxidation at these oxygen pressures.

At still higher temperature (800 K for 0%-Pt and 10%-Pt, 700 K for 20%-Pt), the concentration of aluminum oxide begins to fall. Other authors have reported the complete disappearance of metastable aluminum oxide from NiA1 and Ni₃Al surfaces in UHV at high-temperatures, 1100 K to 1500 K [15,17,48,49,56]. Thermal instability of Al_xO_y has been observed on other metal substrates as well, including pure Al, at temperatures as low as 1000 K [57–59]. Two interpretations have been given: Desorption [59] or dissolution [57] of oxygen. This occurs well below the melting point of bulk α -Al₂O₃, 2345 K [15].

The LEIS data of Fig. 8 show that as the oxide disappears at high-temperature, the islands of Al_xO_y shrink laterally, not vertically. This is reminiscent of results from Bardi et al. [10], who concluded that during the reverse process—growth—island thickness remains constant, at least on the binary Ni₃Al surface.

5. Conclusions

One main effect on oxidation of adding Pt to Ni₃Al revealed by this work is that Pt reduces the NiO content. This is consistent with the suppression of nickel oxides (both NiO and NiAl₂O₄) observed in previous work conducted at much higher temperatures and pressures. The explanation for both may simply be a reduction in the availability of Ni. (This explanation may also account for the decrease in sticking coefficient in the presence of Pt, in our data.) An effect for which we have no explanation at present, however, is the reduction in the amount of Al_xO_y formed in the presence of Pt. Another main effect is the shift in Al_xO_y growth to lower temperatures, which is consistent with a

Pt-induced increase in the rate of diffusion of Al from the bulk, to form surface Al_xO_y . Importantly, the effects of Pt revealed in this study are consistent with proposed explanations of its effects under more technologically-relevant oxidizing conditions [7,9].

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