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Correlations between structure and chemical composition on oxidized $(Pt, Ni)_3Al(1\,1\,1)$ surfaces

F. Qin [a,b], B. Hunt [b], B. Unal [a,c], D. Jing [a,b], M. Shen [b], C.J. Jenks [a], B. Gleeson [a,c,1], D.J. Sordelet [a], P.A. Thiel [a,b,c,*]

[a] *Ames Laboratory, Iowa State University, Ames, IA 50011, USA*
[b] *Department of Chemistry, Iowa State University, Ames, IA 50011, USA*
[c] *Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA*

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Abstract

We have investigated the fully-oxidized surface that forms on $(Pt, Ni)_3Al(1\,1\,1)$ at temperatures ranging from 300 to 1000 K and at oxygen pressures of *ca.* 10^{-6} to 10^{-7} Torr, using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Based on X-ray photoelectron spectroscopy data that were published previously, oxidation temperatures below 700 K at these pressures produces a mixture of surface Al_2O_3 and NiO, with NiO being the predominant oxide. At 800–1000 K, pure Al_2O_3 exists. In this work, STM data from a sample containing 10 at% Pt show that oxidation causes an increase in roughness, relative to the clean surface. The apparent roughness correlates directly with NiO content, both of which reach a maximum at an oxidation temperature of 500 K. The oxide surface is smoothest when it consists of pure Al_2O_3, i.e. after oxidation at 800–1000 K. In terms of crystallinity, LEED data show that the Al_2O_3 which forms at 1000 K is ordered, but its structure on the Pt-containing samples is different than reported previously for the Pt-free surface. This is true despite the structure of the clean surface being unperturbed by Pt, based on STM and LEED. The different structure of the oxide probably relates to the fact that the oxide is also thinner in the presence of Pt. The change in oxide structure undoubtedly correlates with a change in stability and adhesion of the oxide, both of which are of paramount importance in industrial applications.

Keywords: Oxidation; Nickel aluminide; Platinum; Scanning tunneling microscopy; Low-energy electron diffraction (LEED)

1. Introduction

The intermetallic compound Ni_3Al is of significant technological importance because of its high strength combined with its excellent oxidation resistance at high temperature [1–3]. To gain basic insight into its oxidation resistance, the interaction of clean Ni_3Al with oxygen at low oxygen pressures (ca. 10^{-8} to 10^{-6} Torr) has been studied extensively [4–20]. When the sample is oxidized below about 700 K, an amorphous mixture of alumina and NiO develops, with the alumina on top of the NiO. A pure, crystalline Al_2O_3 layer develops when the sample is oxidized at higher temperatures [8–10,12,13,15–19]. (A third phase, spinel or $Ni_2Al_4O_6$, can also develop when Ni_3Al is oxidized at higher pressures [21–23].) The observation of two different phase mixtures in two different temperature regimes [5,6] reflects the fact that nickel oxides are kinetically-favored, whereas aluminum oxide is thermodynamically-favored. The transition at 700 K marks the onset of long-range diffusion of Al between the bulk and surface, which is necessary for formation of the thermodynamically-favored phase, on the time scale of oxidation at 10^{-8} to 10^{-6} Torr [4,20].

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[*] Corresponding author. Address: Ames Laboratory, Iowa State University, Ames, IA 50011, USA. Tel.: +1 515 294 8985; fax: +1 515 294 6789.
E-mail address: pthiel@iastate.edu (P.A. Thiel).

[1] Present address: Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA.

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Recent work has indicated that adding Pt to Ni_3Al can significantly improve the oxidation resistance of this material at high temperatures because Pt promotes the preferential formation of an adhesive Al_2O_3-rich scale in air [24–26]. To understand how Pt addition induces this beneficial effect, a basic starting point is again to investigate the interaction of oxygen with the clean surface at low oxygen pressure within the confines of an ultra-high vacuum (UHV) chamber [20,27]. Using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and low-energy ion scattering (LEIS), we recently investigated the chemical nature and depth distribution of the oxide that forms upon saturation at an oxygen pressure of 10^{-7} Torr, in the temperature range 300–900 K [20]. We found that the effect of Pt was to reduce the amount of both oxides at all temperatures, and to lower the temperature needed to establish the pure Al oxide layer by about 200 K.

Other aspects of the structure of the oxidic overlayer that forms on a clean metal surface, such as its topography and its crystal structure, are also important. Wandelt and co-workers [8,10–13,15–18] and Schmid et al. [19] have studied the interaction of oxygen with $Ni_3Al(111)$ at temperatures ranging from 300 to 1000 K using scanning tunneling microscopy (STM), high resolution electron energy loss spectroscopy (HREELS) and low-energy electron diffraction (LEED). There is no analogous study, of which we are aware, for $(Pt,Ni)_3Al(111)$. The aim of this work is to examine the fully-oxidized $(Pt,Ni)_3Al(111)$ surface after oxidation at temperatures between 300 and 1000 K using STM and LEED. Emphasis is placed on the apparent roughness and crystallinity of the oxides. It turns out that Pt promotes a different type of epitaxial orientation of Al_2O_3 at 1000 K, which may be related to our previous observation [20] that Pt reduces the amount of Al_2O_3 at high temperature. Another interesting result is that the apparent surface roughness correlates directly with NiO content; the Al_2O_3 is relatively smooth.

The clean surface that forms the starting point for UHV oxidation is well-characterized. The binary alloy Ni_3Al crystallizes in a face-centered cubic (fcc) lattice, and the (111)-plane shows a bulk-like termination. The structure of $Ni_3Al(111)$ has been deduced from dynamical LEED analyses [28], and atomically-resolved STM images have been reported by several groups [9,10,19,29,30]. The chemical order in the bulk is preserved at the surface, such that the surface is sometimes described as a (2×2) arrangement of Al atoms. Its structure can be viewed in Fig. 1 of either Ref. [8] or Ref. [10]. The surface unit cell length is 0.50 nm [9,10]. For the ternary, Pt-containing alloy, previous density functional theory (DFT) calculations [31,32] and experimental studies [25,26] indicated that Pt substitutes for Ni in the bulk. At the surface, Pt tends to segregate and leads to some disorder [33,34]. However, it does not destroy the geometrical surface structure, at least up to a bulk concentration of 20 at% Pt (surface concentration up to 26 at% Pt), as judged by LEED [33,34].

2. Experimental description

The STM experiments were performed in a UHV chamber equipped with a variety of probes [35]. LEED experiments were carried out in a separate chamber, on parallel sets of samples. The base pressure was 2×10^{-11} Torr and 9×10^{-11} Torr in the STM and LEED chamber, respectively. Exposures are reported in terms of Langmuir ($1\ \mathrm{L} \equiv 10^{-6}$ Torr s). Oxygen exposure was achieved by backfilling the STM and LEED chambers with research grade oxygen (99.99%) to a constant pressure of 1×10^{-6} Torr and 2×10^{-7} Torr, respectively. An exposure of about 1200 L was sufficient to saturate the surface with oxygen in both chambers, based upon AES. After oxidation, the sample was cooled to room temperature before making STM and LEED measurements.

Only a single Ni_3Al sample, containing 10 at% Pt (hereafter called 10%-Pt) was studied with the STM. Two samples were examined with LEED: a different 10%-Pt sample, and another containing 20 at% Pt (called 20%-Pt). Large 10%-Pt and 20%-Pt single crystal ingots were prepared using the Bridgman technique by the Materials Preparation Center at the Ames Laboratory [36]. Both samples were oriented and sectioned from the ingot by electrical discharge machining. Surfaces were oriented to within ±0.25° accuracy of the (111) orientation, then polished using standard metallographic techniques. The samples were cleaned in UHV in both chambers by repeated cycles of Ar^+ sputtering followed by annealing to 1100 K for 1 h, until the surfaces were judged clean with AES, LEED and STM (if available).

3. Experimental results and interpretation

3.1. STM: clean surface

Fig. 1a shows an atomically-resolved STM image (10 nm × 10 nm) of the clean 10%-Pt $Ni_3Al(111)$ surface. Fig. 1b displays the profile for the line in Fig. 1a. The image reveals a hexagonal array of features with an average separation of 0.50 ± 0.01 nm. The value of 0.50 nm agrees with the separation measured on the surface of Pt-free $Ni_3Al(111)$ [9,10] and also with the bulk lattice constant of the Pt-free alloy, 0.50 nm. Therefore, the addition of 10 at% Pt does not change the in-plane lattice constant of $Ni_3Al(111)$. Furthermore, our previous LEED study [33], showed that the surface lattice constants for 10%-Pt and 20%-Pt samples are the same within ±0.8%. Therefore, Pt concentrations in the range 10–20 at% have no measurable effect on the lateral crystal structure.

A larger-scale STM image of the clean 10%-Pt surface is shown in Fig. 2a. The terrace width is 20–120 nm. The clean sample is flat on a nanoscopic scale, with a step height of 0.203 ± 0.015 nm. This is in agreement with expectation for the Pt-free alloy, $Ni_3Al(111)$, where a previous measurement yielded 0.2 nm [9] and where the bulk interplanar spacing is 0.206 nm. Therefore, the presence