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# Field ion microscopy of platinum adatoms deposited on a thin $Al_2O_3$ film on NiAl(1 1 0)

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#### Abstract

Aiming to contribute to a characterisation of the surface diffusion and clustering of individual metal adatoms on a well-characterised oxide film the feasibility of FIM investigations is demonstrated for the catalytically relevant system  $Pt/Al_2O_3/NiAl(1\ 1\ 0)$ . A thin aluminium oxide film was grown on a [110] oriented NiAl field emitter through dissociative oxygen adsorption followed by heating cycles. The film was characterised using FEM, FES and neon FIM. Field desorption sequences revealed that the film prepared on NiAl(110) was approximately two layers thick. Below 80 K the film was stable at field-strengths applied for neon FIM. The presence of an ordered structure was suggested by FEM and FIM pattern. FIM of Pt adatoms was achieved at 79 K and below best image field strength using neon as the imaging gas. From preliminary displacement observations the surface diffusion activation energy of individual Pt adatoms was estimated and ranges between 0.4 and 0.5 eV. After three heating cycles to a maximum temperature of 230 K an ordered arrangement of Pt adatoms was noticed in the vicinity of a presumable point defect. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Thin oxide films, supporting small metal aggregates, are of great technological importance since they can act as model systems for heterogeneous catalysis [1,2]. Following a relatively early report [3] on the structural characterisation of an ordered aluminium oxide on NiAl(1 1 0) a series of investigations was carried out on this system using the arsenal of modern surface science techniques including high-resolution imaging methods, such as HREM and STM. Charging effects limit the application of most surface physics techniques to extremely thin films which can be produced in different ways. When the surface of a NiAl crystal is exposed to oxygen the formation of an alumina film is thermodynamically strongly favoured at proper conditions. Structural and electronic properties of such aluminium oxide films have been established, especially for the closed packed NiAl(1 1 0) surface. In this case a well ordered and approximately 0.5 nm thin aluminium oxide film can be grown [2]. The various experimental results obtained suggest that the stoichiometry and the structure of the oxide is compatible with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A schematic structure model of the oxide film is sketched in Fig. 1.

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Fig. 1. Schematic structure model of the aluminium oxide film on NiAl( $1 \ 1 \ 0$ ) [2]. Unit meshes of domains A and B of the thin oxide film are shown. The rectangle in the middle illustrates the symmetry of the NiAl( $1 \ 1 \ 0$ ) substrate surface and the distorted hexagon indicates the arrangement of oxygen ions in domain B of the alumina film.

In the field emission community attempts on the preparation and characterisation of metals on less ordered and relatively thick oxides, such as Ni/Rh<sub>2</sub>O<sub>3</sub> [4] and Pd-Mo/Al<sub>2</sub>O<sub>3</sub>/W have been reported [5]. Using an atom probe FIM the oxidation of a Ni-rich NiAl alloy has been characterised. However, no ordering of the oxide film was reported [6]. We are not aware of any reports on FIM, HREM and STM observations of individual metal adatoms deposited on a well-ordered oxide. Aiming at the study of the energetics and kinetics of the diffusion and clustering of individual metal adatoms on an ordered oxide film we have applied FIM and field electron spectroscopic techniques on the system  $Al_2O_3$  on NiAl(1 1 0). The main goal of the present work has been: (i) preparation and characterisation of an ordered Al<sub>2</sub>O<sub>3</sub> film on a [110] oriented NiAl tip and (ii) FIM of Pt adatoms deposited on the alumina film.

# 2. Experimental procedures

The thin oxide film has been prepared according to previously described procedures [7]. The NiAl tips used as substrates for the oxidation process were produced in four steps: (i) Cutting of [1 1 0] oriented rods from a single crystal, (ii) cleaning of the rods through heating in UHV, (iii) electrolytic etching in air and finally (iv) preparation of the tip in an FIM set-up through heating cycles (to a maximum temperature of 1300 K), neon-ion sputtering and field evaporation. Pulsed FEV at T = 50 K has been employed which should reduce the effect of a preferential removal of aluminium ions [8] deteriorating the formation of an alumina film during oxidation. For preparation of the aluminium oxide layer the cleanliness of the NiAl tips was checked, e.g. through a final FEM picture before dosing the tip with  $O_2$ . At the initial stage of the experiments the dose was 1500 L at 350 K guided by earlier measurements [7,9]. After measurements of oxygen induced work function changes on NiAl(110), we increased the doses in order to secure a complete O coverage at 350 K. An ordered alumina film was formed through a number of thermal flashes (to a maximum temperature of 1300 K) and after each single flash an electron current measurement was taken accompanied by an FEM picture. When the electron current remained constant the oxide film was imaged in neon. Eventually, the film was field evaporated producing a clean NiAl-substrate surface followed by a new preparation sequence.

Two FIM/FEM set ups have been used. The first one allowed liquid-nitrogen cooling of the specimen [10] and has been equipped with a platinum

evaporator. It was built using a heatable tungsten loop which was covered with a small piece of platinum wire. After several outgassing cycles the Pt flux was calibrated using a tungsten tip. The vacuum was improved through an additional sublimation pump so that a base pressures below  $10^{-11}$  mbar was reached. After exploratory FIM on Pt/Al<sub>2</sub>O<sub>3</sub>/NiAl(110) at 79 K a new specimen holder was installed allowing gaseous or liquid helium cooling of the specimen. FIM at 50 K was thus made possible leading to significantly improved image qualities. For probe hole FIM/FEM measurements a second set-up allowed field-ion and electron spectroscopy of selected surface sites [11]. Energy analyses were carried out in a retarding potential and a hemispherical mirror analyser. The latter was especially used for measurements of the low energy side of electron energy distributions. From energy distribution and i-V (Fowler-Nordheim) measurements work function data of NiAl(1 1 0) were determined [12].

# 3. Results and discussion

To convey an impression of the results of the preparation procedures we present observations of the clean and of the oxidised NiAl tip. The images shown in Fig. 2 have been obtained at T(NiAl) = 50 K allowing neon FIM at good resolution and contrast conditions. Pulsed FEV has been employed for cleaning the specimen surface using a pulse to DC fraction of more than 20% but not exceeding 40%. In the example shown in Fig. 2(a) a pulse voltage of 3.2 kV was superimposed on a DC voltage of 8 kV in order to minimise the



Fig. 2. (a) Neon FIM of [1 1 0] oriented NiAl prepared by pulsed FEV at 50 K. (b) After flashing to 1300 K the diameter of the (1 1 0) plane has increased by one order of magnitude to approx. 50 nm. (c) After oxidation followed by FD an aluminium oxide island is left on the NiAl(1 1 0) apex plane. (d) The FEM pattern shows CsCl (bcc-like) symmetry and the boundary of the oxide island. The dead spot has been produced by an inactive area in the channel plate.

effect of preferential FEV of aluminium ions. One can also restore the surface concentration of Al by flashes to 1300 K as will further be discussed below. Our observations show that flashing to this temperature does not blunt the tip. We have routinely used this technique to approach the thermal end form. Fig. 2(b) shows the shape of a thermally prepared tip characterised by an enlarged (1 1 0) plane. Compared to a low-temperature FEV shape a thermally enlarged NiAl(1 1 0) facet can of course be covered by a larger number of Al<sub>2</sub>O<sub>3</sub> unit cells.

The oxide film was formed applying a procedure which included dissociative O<sub>2</sub> adsorption and flash heating to temperatures ranging between 700 K and 1300 K [7]. FIM observations during field desorption revealed that the oxide film covering the (1 1 0) facet was approximately two layers thick. It was stable in high field conditions needed temperature (<80 K)low neon for FIM ( $\approx$  33 V/nm). It could be "peeled off" from the surface in a controlled manner through field desorption. The layer on the NiAl(1 1 0) apex plane came off at the end and showed greatest stability. Oxide islands of a desired size as in Fig. 2(c) and (d) can routinely be prepared now. The oxide showed some amount of order as deduced from FIM and FEM observations. The boundary between the oxide island and the NiAl substrate could clearly be visualised even in the FEM pattern in Fig. 2(d). In view of the experience assembled for metal substrates, such oxide islands should be well suited for FIM studies of the diffusion of adatoms such as platinum.

To further characterise the clean and the oxidised NiAl(1 1 0) surface we have carried out probe hole FEM analyses. Fig. 3 shows the results of i-V and total energy distribution measurements for electrons field emitted from the centre of a NiAl(1 1 0) plane prepared by DC FEV at 79 K. Work function data derived from such measurements [12] for different pretreatments are given in Table 1. A thermal flash to 1300 K reduces the work function of those NiAl(1 1 0) surfaces which had been prepared by DC FEV at 79 K. This change agrees with earlier photo emission data on macroscopic NiAl(1 1 0) samples correlating the decreasing work function with a shift in the stoichiometry to the ideal 50%Ni/50%Al ratio [13].

Fig. 4 shows field electron energy spectra derived from retarding potential analyses of clean, O-covered



Fig. 3. Probe-hole FEM analyses of clean [1 1 0] oriented NiAl. (a) Two Fowler-Nordheim (FN) plots and (b) one total energy distribution are shown. From the slopes,  $m_{\text{FN}}(1 \ 1 \ 0)$  and  $m_{\text{ED}}(1 \ 1 \ 0)$  work function values of NiAl(1 1 0) are obtained. Values for  $m_{\text{FN}}(\text{total})$  were derived from measurements of the total current through the tip.

and oxidised NiAl(110). The spectra showed onsets at the Fermi level which were identical within 30 meV for the clean NiAl(110) and the oxidised surface in agreement with the result of an earlier FES measurement [14]. We conclude that the thin  $Al_2O_3$  film is highly transparent for electrons of the NiAl substrate at the Fermi energy in an applied electric field of approx. 4 V/nm. It should be noted that the field emission current in Fig. 4(a) has decreased by approximately a factor of two after the oxide growth had been completed on NiAl(110). Exposing a thermally cleaned NiAl(110), as in Fig. 4(a) to 6000 L O<sub>2</sub> at T(NiAl) =350 K, lowers the local emission current by a factor of 30. This is interpreted as a significant work function increase possibly caused by chemisorbed oxygen. A partial oxidation of the NiAl(110) surface can also not be excluded [9]. In conclusion, the

Table 1 Work function data of clean NiAl

Pretreatment	Work function (eV)		
	(1 1 0)	Total	
d.c. FEV, 79 K Flash, 1300 K	5.6 5.1	4.5	

probe hole FEM approach gives valuable data which are particularly helpful for the procedures involved in the preparation of the oxide film.

Finally, we report the results of our attempts to image individual platin adatoms deposited on the oxide film at 79 K using neon FIM. The best image field strength was not applied since the film already started to field desorb at 79 K at that condition. This was verified after the adatom imaging sequence had been finished. For these reasons neon FIM was characterised by strong fluctuations and non-optimum contrast. These drawbacks could partly be compensated by computer aided superposition of selected video frames. The contrast reversed pattern in Fig. 5(a) has been obtained by superposing 44 single frames taken at 9.0 and 9.5 kV, Neon-BIV  $\approx$  10.7 kV, FEV(NiAl)  $\approx$  12.6 kV,  $FD(Al_2O_3/NiAl(110)) \approx 10.6 \text{ kV}$  at 79 K. This procedure al-lowed to visualise weak features, such as the ones located on the boundary of the uppermost oxide layer. Four emission centres located on the topmost Al<sub>2</sub>O<sub>3</sub> plane could be identified. Since field desorption of the oxide film even in peripheral regions of tip was avoided in this particular experiment, the origin of the four emission centres on the bare alumina substrate remains obscure. It is conceivable that these spots are images of locally protruding substrate atoms. Alternatively, one could



Fig. 4. (a) Retardation curves of field emitted electrons were measured for clean and oxidised NiAl( $1\ 1\ 0$ ) and for the surface covered with a saturation layer of chemisorbed oxygen. (b) Electron energy distributions have been obtained by differentiation. At the Fermi energy the shift of the onsets for clean and oxidised NiAl( $1\ 1\ 0$ ) is within the experimental uncertainty (30 meV).



Fig. 5. Neon FIM of  $Pt/Al_2O_3/NiAl(1 \ 1 \ 0)$  at 79 K. Time-averaged video frames displayed in negative contrast mode show the surface of the aluminium oxide film: (a) Before and (b) after deposition of platinum. Images (a) and (b) were obtained from FIM observations at applied voltages between 9.0 kV and 9.5 kV (Neon BIV  $\approx 10.7 \text{ kV}$ ). The polygon curves indicate the boundary of the topmost  $Al_2O_3$  layer (diameter ca. 25 nm). (c) After three heating cycles of approx. 10 s at 200–230 K, neon FIM was done at higher applied voltage, 9.9 kV (FD ( $Al_2O_3$ )  $\approx 10.6 \text{ kV}$ )). (d) A model has been outlined for positions of Pt adatoms locally arranged, close to a presumble defect site (arrow).

presume the presence of point defects such as single adatoms on an otherwise perfect  $Al_2O_3$  surface.

Intending to observe cluster formation of platinum adatoms, the oxide surface was exposed to a relatively high platinum dose at field free conditions and at  $T(Al_2O_3) = 79$  K. The dose (offered for 3 min) had earlier been calibrated by means of a [1 1 0] oriented tungsten tip and amounted to approx. 15 Pt atoms per  $Al_2O_3$  unit cell, 1.9 nm<sup>2</sup> as sketched in Fig. 1. After Pt deposition the FIM pattern in Fig. 5(b) was obtained at the same applied voltages as in Fig. 5(a). Thirty spots can be counted, some of which have already been identified at 8.8 kV. These spots are located within the polygon curve indicating the boundary of the topmost oxide plane of the tip apex. Nine additional spots located very close to the boundary have been discarded. The imaged objects represent most probably individual Pt adatoms. On the basis of earlier experiences [2] exchange with substrate atoms and interdiffusion processes through the film are excluded for present deposition conditions  $(T(Al_2O_3) = 79 \text{ K})$ . The counted number of spots (30) gives only a lower limit of the actual number of deposited Pt atoms since the applied electric field strength was not high enough to identify all adatoms, at least at this stage of the experiment. Almost all spots observed after Pt deposition appear to provide images of individual adatoms. One exception is a possible dimer configuration spotted at approx. ten o'clock in Fig. 5(b).

In spite of limitations governing the imaging process at 79 K, we have obtained first hints on the local ordering of Pt adatoms. This was visualised at somewhat higher applied voltage, 9.9 kV which was still well below the desorption voltage for the oxide film, 10.6 kV. After three heating periods of approx. 10 s at 200–230 K ordering occurred in the vicinity of a presumable defect site close to the step edge (Fig. 5(c)). We can not exclude that adatoms had crossed the step-boundary of the uppermost layer (in both directions), especially during the last heating step when the surface temperature reached 230 K. At this temperature (and above) we observed a significantly changing total number of adatoms on the topmost plane. For an examination of the energetic properties of the step edges more single adatom experiments are desirable. Since the variation of the magnification has not been mapped out a reliable distance calibration can not be given at present. In view of our current experimental analyses we favour a calibration which would result in a unit mesh distance (Fig. 5(d)) of approx. 0.6 nm. This implies a local arrangement of the Pt adatoms characterised by a relatively open structure. It is striking, however, that the alignment of the adatoms is compatible with directions given by the long and the short axis of the Al<sub>2</sub>O<sub>3</sub> unit cell of domain B (Fig. 1).

To initiate surface diffusion of the Pt adatoms the oxide was heated four times: (i) 200 K 10 s (ii) 220 K 13 s (ii) 230 K 10 s and (iv) 240 K 10 s at field free conditions. From the FIM observations made before and after (i) we conclude that the adatoms start to jump already at 200 K (and possibly at an even lower temperature<sup>1</sup>). From FIM images of the clean NiAl tip, taken before oxide preparation and after removal by FD, we got a rough estimate of the diameter of the topmost oxide plane in Fig. 5 of approx. 25 nm. Using this calibration we determined minimum and maximum values for adatom displacements allowing to estimate values of the

Table 2 Estimation of surface diffusion parameter for  $Pt/Al_2O_3/Ni(1\ 1\ 0)^a$ 

Displacement (nm)	Diffusivity (nm <sup>2</sup> /s)	Activation energy (eV)
0.8	0.014	0.51
24	15	0.39

<sup>a</sup> T = 200 K, t = 10 s.

activation energy of surface diffusion. For an estimate of the (2-dim. random walk) diffusivity,

$$D = D_0 \exp\left(-E_{\rm d}/kT\right) = \langle r^2 \rangle/4t,\tag{1}$$

a value for the prefactor has been calculated, using the relation

$$D_0 \approx 0.25 l^2 k T/h. \tag{2}$$

Here,  $E_d$  is the activation energy of surface diffusion, k and h are Boltzmann's and Planck's constants. Minimum and maximum values for the mean square displacement  $\langle r^2 \rangle$  were obtained from present FIM observations. The elementary diffusion length, l was assumed as 0.3 nm as suggested by the surface structure of Al<sub>2</sub>O<sub>3</sub>/NiAl(1 1 0) shown in Fig. 1. Numerical values of the estimated surface diffusion parameter are given in Table 2. It is clear, however, that a precise experimental determination of surface diffusion parameter requires more accurate measurements of the displacement, especially at different surface temperatures.

## 4. Conclusion

It appears feasible that selected, relatively strongly bound adatom species, deposited on a thin  $Al_2O_3$  film on NiAl(1 1 0) can be imaged by low temperature neon FIM as verified for Pt in experiments at 79 K. From the present FIM observations we conclude that Pt adatoms are quite mobile at 200 K and start to jump at a significantly lower temperature. Experiments carried out below 50 K should improve the conditions for FIM of Pt/Al\_2O\_3/NiAl(1 1 0) thus allowing to characterise surface diffusion properties of individual platinum adatoms in more detail.

<sup>&</sup>lt;sup>1</sup> Recently, two of us (G.B. and N.E.) measured the onset temperature for the surface diffusion of three Pt adatoms deposited on Al<sub>2</sub>O<sub>3</sub>/NiAl(1 1 0) employing Neon-FIM at 45 K:  $T_{onset} = 165$  K. Using Eqs. (1) and (2) one obtains a value for the surface diffusion activation energy,  $E_d \approx 0.45$  eV ( $D_0 = 7.7 \times 10^{-4}$  cm<sup>2</sup>/s, T = 165 K,  $\langle r^2 \rangle = 9 \times 10^{-16}$  cm<sup>2</sup>, t = 20 s,  $l = 3 \times 10^{-8}$  cm).

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