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Surface dynamics dominated by bulk thermal defects: The case of NiAl(110)

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We find that small temperature changes cause steps on the NiAl(110) surface to move. We show that this step motion occurs because mass is transferred between the bulk and the surface as the concentration of bulk thermal defects (i.e., vacancies) changes with temperature. Since the change in an island's area with a temperature change is found to scale strictly with the island's step length, the thermally generated defects are created (annihilated) very near the surface steps. To quantify the bulk/surface exchange, we oscillate the sample temperature and measure the amplitude and phase lag of the system response, i.e., the change in an island's area normalized to its perimeter. Using a one-dimensional model of defect diffusion through the bulk in a direction perpendicular to the surface, we determine the migration and formation energies of the bulk thermal defects. During surface smoothing, we show that there is no flow of material between islands on the same terrace and that all islands in a stack shrink at the same rate. We conclude that smoothing occurs by mass transport through the bulk of the crystal rather than via surface diffusion. Based on the measured relative sizes of the activation energies for island decay, defect migration, and defect formation, we show that attachment/detachment at the steps is the rate-limiting step in smoothing.

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I. INTRODUCTION

Mass transport through the bulk of crystalline solids commonly occurs by vacancy diffusion.[1] While solid surfaces are well known to act as sinks and sources for bulk thermal defects such as vacancies,[2] there are few observations that actually reveal how defects are annihilated or created at surfaces. With low-energy electron microscopy (LEEM), surfaces can be imaged at temperatures high enough that bulk defects exchange with the surface at a significant rate. In this paper, we use this capability to show where the creation and annihilation of bulk thermal defects occurs on the (110) surface of NiAl.

Another reason for being interested in atomic bulk/surface exchange is that bulk defects have long been recognized to enable a surface to reduce its free energy by smoothing.[3,4] In the early days of ultrahigh vacuum, surface-science experiments performed on simple metals near their melting points concluded that mass diffusing through the bulk via bulk defects could dominate the smoothing.[5–8] Despite this awareness that bulk defects could have a large influence on surface morphology, most recent theoretical[9–21] and experimental[21–43] work on the morphology evolution of surfaces emphasized processes that occur in the outer one or two layers. In part, this emphasis occurred because scanning tunneling microscopy can readily characterize atomic step motion at the low temperatures where surface diffusion dominates surface evolution. LEEM offers the advantage of often being able to observe easily the motion of atomic surface steps in real time at higher temperature.[44] Using this capability, we will show that bulk defects control surface smoothing on NiAl.

NiAl is an ordered intermetallic alloy that has been extensively studied by experiment and theory.[45] Its (110) surface has a nearly bulklike termination, with only a slight buckling of atoms out of the surface plane, and does not reconstruct.[46] We have recently presented a short report[47] describing the relationship between bulk defects and the surface dynamics of NiAl as observed by LEEM.[44] We found that the bulk defects dominate the surface dynamics of NiAl—significant mass was transferred to and from the surface as temperature was varied, and the smoothing of surface morphology occurred by bulk atomic transport.

Since our report, the importance of bulk thermal defects on the surface dynamics of other materials has been directly observed. The ceramic material TiO_2 also exhibits mass flow between the surface and the bulk when the temperature is changed.[48] This bulk-defect-driven mass flow was shown to greatly accelerate a phase transition on the $TiO_2(110)$ surface. This transition changes both the surface's structure and stoichiometry.[49,50] Similar mass flow resulting from the temperature dependence of bulk thermal defects has been directly observed for Pt.[51] Recent analysis has also shown that the mass diffusion responsible for step fluctuations on the Pt(111) surface, at sufficiently high temperature, occurs primarily by diffusion through the bulk, not across the surface.[52] Finally, mass flow between the bulk of a TiN thin film and its surface has also been recently observed.[53] In contrast to NiAl, TiO_2, and Pt, where the mass flow causes all steps to move, the mass flow in TiN was only observed near surface-terminated dislocations. The generality of this phenomena motives work to characterize the temperature-change-driven mass transport in more detail.

To reinforce our previous conclusions, we present here more complete observations regarding the role of bulk thermal defects on the surface dynamics of NiAl. After describing the experimental procedure, we show that steps of all curvature (positive, negative, and nearly straight) move when NiAl's temperature is changed. We then show that the magnitude of step motion is so large that it can only result from a mass flow between the bulk and the surface. We also show that steps originating from surface-terminated bulk dislocations move during temperature changes, but that the mass transport between the surface and the bulk is not enhanced along the bulk dislocations. After presenting and justifying an analytical model of the bulk/surface mass flow, we go on to show how this model can measure the formation and migration energies of the bulk thermal defects. Finally, we discuss the role of bulk thermal defects in surface smoothing.

II. EXPERIMENTAL PROCEDURE

The NiAl(110) surface was prepared by sputtering with 500-eV Ar ions and annealing to about 1200 K. Because of preferential loss of Al during the many annealings, the crystal became enriched in Ni to a composition of $Ni_{57}Al_{43}$ as measured by wavelength-dispersive electron microprobe analysis. Temperatures were measured using a W–26%Re/W–5%Re thermocouple that was spot welded to the side of the crystal. The base pressure of the LEEM vacuum chamber was below 10^{-10} Torr. Even while imaging at high temperatures the pressure was below 10^{-9} Torr and was typically in the mid to low 10^{-10} Torr range. Images were formed from the specularly reflected electron beam (i.e., in bright-field mode) with an electron energy of 3.8 V. These conditions produce a large contrast at surface steps.[54] Determining which of the two terraces next to a step was higher was done by evaporating copper onto the crystal and observing the direction of step motion during step-flow growth.

III. RESULTS AND DISCUSSION

A. Temperature-change-driven mass transport

Figures 1–4 present evidence for a significant flow of mass between NiAl's surface and bulk during a temperature change. That is, steps on the NiAl(110) surface retract and advance when the crystal is cooled or heated, respectively. This effect occurs for steps of all curvatures. Figure 1 shows that nearly straight steps move markedly for a temperature change of only a few degrees. Figure 2 gives an example for a step of negative curvature (a one-atom-deep pit). The pit shrinks in area when the temperature increases and grows when the temperature decreases. The movement of positively curved steps is shown in Fig. 3 as an island stack (a "wedding-cake" structure) is cooled from 958 to 740 °C. Four layers are removed from the entire stack and at least seven layers are removed from the outer regions.[55] Finally, during temperature changes, mass flows reversibly to and from the surface in the vicinity of surface-terminated dislocations. Figure 4 shows a surface step that originates where a bulk dislocation terminates at the surface. As the NiAl crystal cools, the step spiral enlarges, i.e., it adds new step length, as mass flows from the surface to the bulk.

As Fig. 3 illustrates, changing temperature can remove several layers from the NiAl surface. We also observe that moderate temperature increases can add considerable material to the surface. For example, heating by 100 °C causes existing islands in a stack to expand sufficiently in a step-flow mode such that the equivalent of about four layers is added over the breadth of the stack.[56] These large mass flows are not possible for a process limited to the surface layer. Therefore, the mass source and sink must be the bulk. That is, we are directly observing mass being transported between the bulk and the surface.

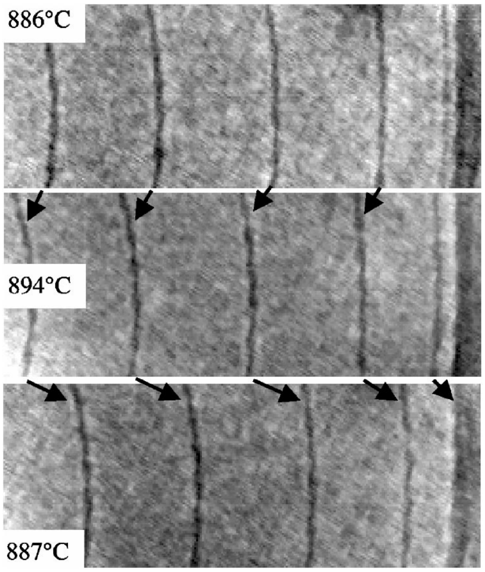

FIG. 1. Low-energy electron microscopy (LEEM) images of the NiAl (110) surface showing how temperature changes move nearly straight steps. The dark lines are the monatomic steps on the surface, which is stepped up from left to right. The step bunch (dark band) at the right serves as a fiducial point for the step position. When heated from 886 °C (top image) to 894 °C (middle image), the steps move in the downhill direction, i.e., the steps advance. When cooled to 887 °C (bottom image), the steps retract. Images are $2.4 \times 0.9\ \mu m^2$.

An important conclusion about the nature of the bulk thermal defects can be made by carefully analyzing the mass flow as it occurs during a temperature change. The band of material added to the surface when a step advances during a

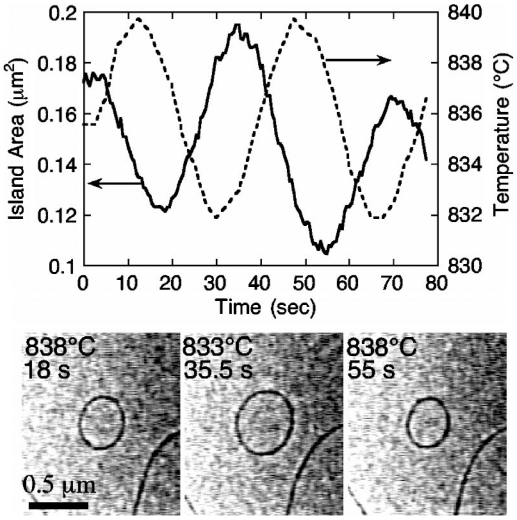

FIG. 2. Effect of temperature on the size of a one-atom-deep pit on the NiAl (110) surface. The plot shows crystal temperature and pit area as a function of time. As the temperature is raised, the pit decreases in area as the step advances. The reverse happens on cooling; the pit increases in area as the step retracts.

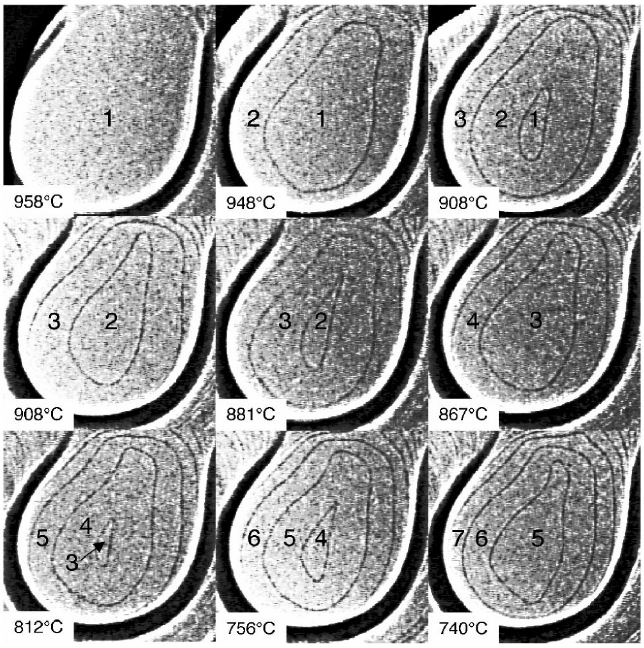

FIG. 3. LEEM images of the NiAl (110) surface as the crystal temperature is lowered in jumps from 958 to 740 °C over an elapsed time of about 2 min. At the initial temperature (upper left image), a single terrace (no. 1) covers the mesa, nearly to its edge. The terraces are labeled in order of decreasing height. After cooling to 740 °C (lower right image), four complete layers have been removed from the entire area of the mesa. Furthermore, near the mesa's edge, at least 7 layers have been removed from the surface. Images are $5\times 5\ \mu m^2$.

temperature increase is indistinguishable from the adjacent surface for all imaging conditions. Also, when a step retracts during a temperature decrease, the band exposed by the retracting step is indistinguishable from the rest of the surface. If the bands had a significantly different composition than the rest of the surface, the surface would convert to another structure. This reconstruction would cause the bands to have an image intensity different from the rest of the surface, giving rise to contrast between the added bands and the rest of the surface. This effect was observed during mass flow from the TiO_2 (110) surface to its bulk.[48] For NiAl, however, we observe no such contrast. Because the composition of the NiAl (110) surface is close to the bulk,[46] these observations establish that the material being exchanged between the surface and the bulk is the alloy with composition close to that of the rest of the surface. Since the material being added to and removed from the surface has the bulk composition, the bulk thermal defects must preserve the stoichiometry of the bulk. We thus directly validate the assumption often made in models of alloy defects.[57–62]

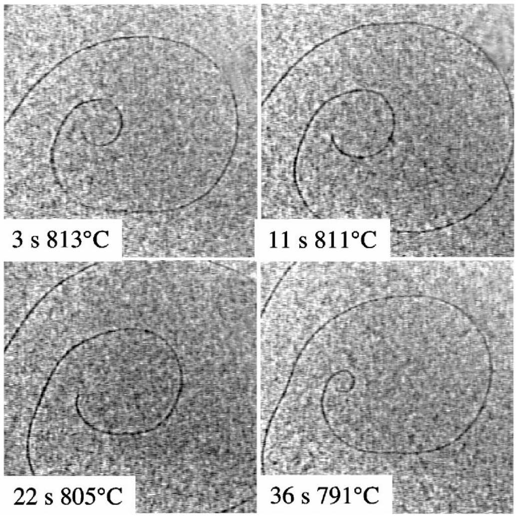

FIG. 4. LEEM images of a step spiral that originates where a bulk dislocation with screw component terminates at the surface. During cooling, the step retracts and the spiral enlarges as mass is transported from the surface to the bulk. Images are $3\times 3\ \mu m^2$.

Because our crystal is Ni-rich ($Ni_{57}Al_{43}$), the dominant zero-temperature defects are believed to be Ni antisites, that is, Ni atoms on the Al sublattice of the cesium chloride structure.[63] The thermal defect consists of two Ni vacancies and an antisite on the Al sublattice, which is collectively referred to as the "triple defect."[57–61,64] Its formation can be viewed as removing two Ni atoms from the bulk Ni sublattice and one Al atom from the bulk Al sublattice. The Al atom and one of the Ni atoms are moved to the surface. Placing the remaining Ni atom on the vacant Al site creates an antisite defect in the bulk. The net process leaves the stoichiometry of the crystal unchanged but moves an NiAl unit from the bulk to the surface:

$$(\mathrm{NiAl})_{\mathrm{bulk}} \Rightarrow 2\mathrm{Ni}_v + \mathrm{Ni}_{\mathrm{Al}} + (\mathrm{NiAl})_{\mathrm{surface}}.$$

Our observations of a temperature-change-driven mass flow of NiAl units between the surface and the bulk is consistent with the triple defect being the most abundant thermal defect. During heating, the bulk increases its triple-defect concentration, causing NiAl to flow from the bulk to the surface. Surface steps advance—that is, islands grow and pits shrink. During cooling, the bulk decreases its triple-defect concentration when NiAl units flow from the surface to the bulk. Surface steps retract, that is, islands shrink and pits grow.

The ability to directly image how thermal defect formation affects surfaces features should allow the defect type to be directly determined as a function of temperature. For example, the thermal defects in Al-rich NiAl are predicted to change from net vacancy annihilation to net vacancy production with increasing temperature.[61,65] If this is the case, the surface steps would retract instead of advancing with increased temperature. Determining the direction of step motion would allow this prediction to be directly evaluated. We have recently used this approach to show that oxygen vacancies (not titanium interstitials) are the dominant thermal defect in rutile-structure TiO_2.[48]

In our short report,[47] we showed that bulk thermal defects are generated and annihilated near step edges since the defect flux to each step is simply proportional to the step length. Another example of this scaling behavior is given in Fig. 5, which shows an island's size as the temperature is oscillated sinusoidally. The island is slowly shrinking due to thermal smoothing (see Sec. III C). Superimposed on this slow size change are oscillations caused by the temperature changes.

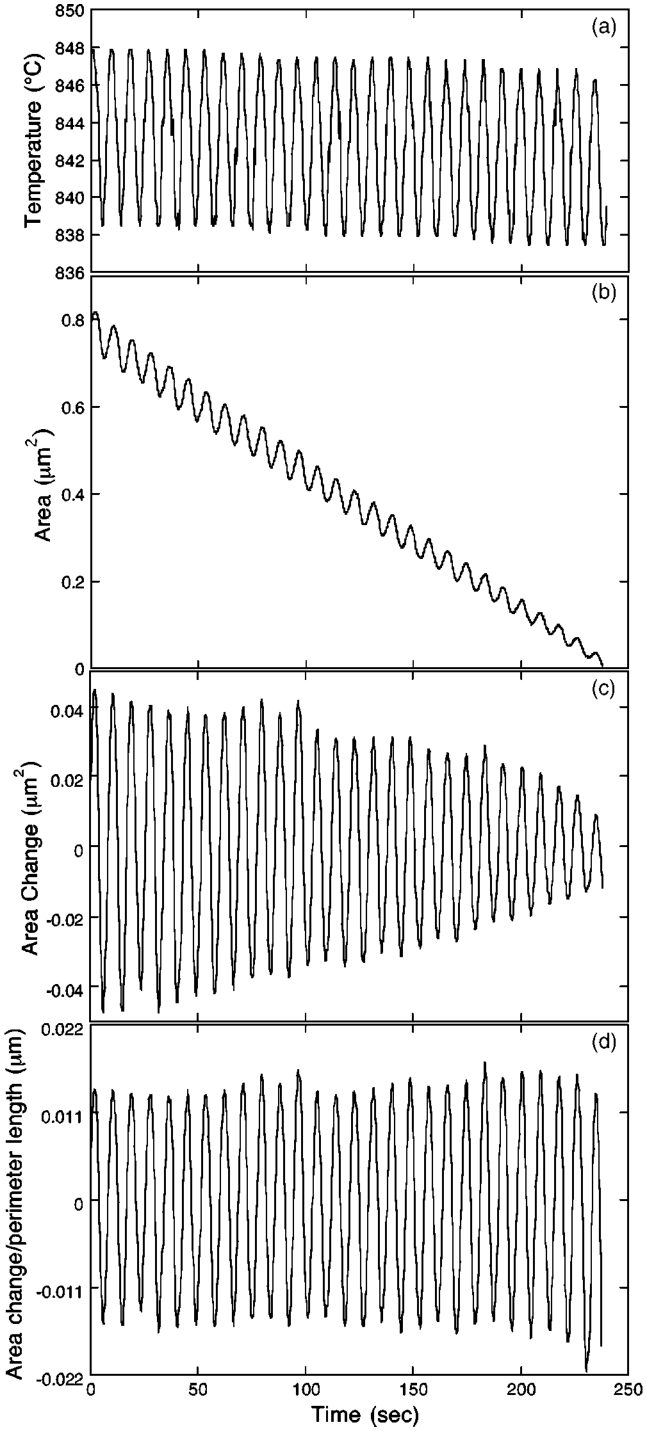

FIG. 5. Effect of temperature oscillation on an island's area. As the temperature (a) is oscillated sinusoidally by ±5 °C around a mean of about 843 °C, the island's area also oscillates (b). This area oscillation is superimposed upon the slow shrinkage of the island resulting from thermal smoothing. Subtracting this nearly linear change in area from plot (b) gives the oscillatory area change function of plot (c). This area change gets smaller as the island shrinks. Dividing the area change by the island's circumference (step length) gives a function of constant amplitude (d) even though the island changed size greatly. This scaling behavior establishes that the bulk thermal defects are created and annihilated only near the steps.

Subtracting the slow decay from the area function gives the area change function [Fig. 5(c)], whose amplitude decreases as the island gets smaller. However, dividing this area change by the island's perimeter gives a function of constant amplitude [Fig. 5(d)]. The remarkably simple conclusion that islands capture and lose atoms simply in proportion to their step length holds for all islands examined at all observed temperatures independent of the island's environment (e.g., density of nearby steps). This establishes that bulk defects are generated only near steps. We emphasize that this is a nontrivial result. While steps are anticipated to be the ultimate source/sink for the bulk defects, it is not obvious that the steps would have controlled the rate at which the bulk defects are created/annihilated. For example, the defects could have been created everywhere on the terraces with the emitted atoms rapidly diffusing to the steps. In this case, each island would change size in proportion to the "capture" area surrounding it.[66]

Importantly, the rate of mass flow was qualitatively the same near dislocations and in dislocation-free (but stepped) regions. In addition, after a temperature change, the mass flow both near dislocations and in dislocation-free regions diminished and stopped at the same time as the crystal equilibrated. This behavior is quite distinct from TiN (111)films[53] where the bulk/surface mass flow only occurred near dislocations, because the dislocations are either the mass source/sink or they act as efficient "pipes" for bulk mass transport. Furthermore, the mass flow coming from TiN dislocations was never observed to diminish (i.e., equilibrium was not achieved), unlike NiAl. We conclude that mass transport is not significantly enhanced along NiAl's bulk dislocations.

To summarize this section, the effect of changing the bulk concentration of thermal defects is directly observed during real-time imaging of surface morphology. For a temperature increase, mass flows from the bulk to the NiAl (110) surface, causing surface steps to advance. We next present a new method of determining the migration and formation energies of the bulk thermal defects based upon driving the crystal's temperature periodically and monitoring how an island's area responds. We begin by showing that a simple one-dimensional model of defect transport through the bulk describes how fluctuations in an island's area depend on the frequency of the temperature oscillations.

B. Model and energetics of bulk/surface mass transport

The frequency of temperature oscillations greatly affects the response of an island's area. If the oscillations are slow enough [Fig. 6(a)], an island's area is nearly in phase with the temperature. As the temperature-oscillation rate increases, the area markedly lags the temperature, and the area oscillations become approximately $\pi/4$ out-of-phase with the temperature [Fig. 6(b)]. In addition, the amplitude of area change is much smaller for the faster oscillation compared to the slow oscillation [Fig. 6(c)].

This frequency dependence can be explained by the following simple model of diffusion toward the surface.[67,68] We first make the assumption (justified below) that the only sig-

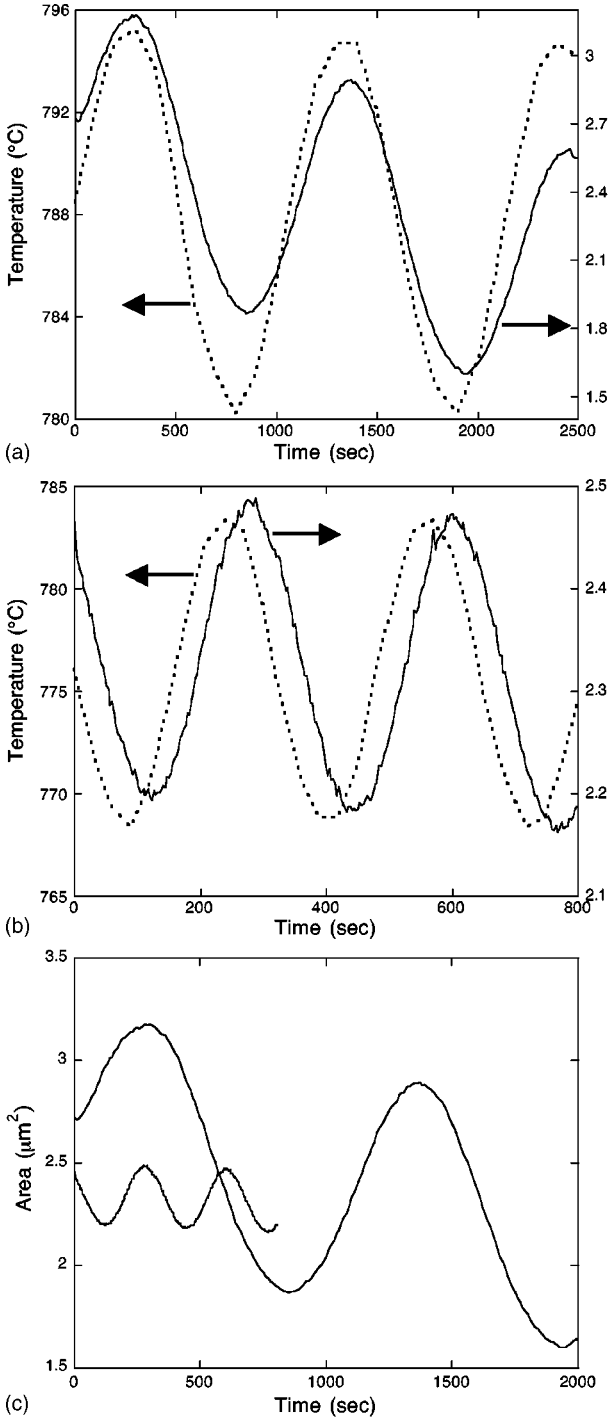

FIG. 6. Effect of oscillation rate on the area change of two similarly sized islands. For the slower oscillation rate of period 1078 s (a), the system response (i.e., the island area) is nearly in phase with the driving function (temperature). For the faster oscillation rate of period 323 s (b), there is a large phase lag between the island area and the temperature. Plot (c) directly shows that the slow temperature oscillations cause a much larger (about 4 times) area change than the faster oscillations. This large difference in response occurs even though the temperature changes were the same and the average temperatures differed only slightly.

nificant gradients in defect concentration are *perpendicular* to the surface. We further assume that the only source and sinks of defects are at the surface. We then solve the one-dimensional (1D) diffusion equation $\partial c_B/\partial t = D\partial^2 c_B/\partial x^2$ for a material slab of width L, where x is the distance perpendicular to the surface, c_B is the concentration of thermal defects, and D is the diffusion coefficient. We emphasize that the D defined by the diffusion equation depends upon temperature but not upon the concentration of thermal defects c_B. Since the surface steps are sources/sinks for bulk thermal defects, the surface, unlike the bulk, rapidly comes into equilibrium after a temperature change. Then, the time-dependent defect concentrations $c_B(x,t)$ at both surfaces are oscillating with the frequency of the temperature oscillation ω: $c_B(\pm L/2, t) = c_0 \cos(\omega t)$. That is, the defect concentration at the surfaces oscillates in phase with the temperature. When the diffusion equation is solved subject to this boundary condition, the flux to the surface F is then found to have a *phase shift* δ with respect to the temperature oscillations:

$$F = -D\left(\frac{\partial c_B}{dx}\right)_{x=L/2} = F_0 \cos(\omega t - \delta), \tag{1}$$

with δ given by

$$\delta(k,L) = \arctan\left[\frac{\sin(kL) + \sinh(kL)}{\sin(kL) - \sinh(kL)}\right] \tag{2}$$

and $k = \sqrt{\omega/2D}$. The normalized flux amplitude F_0/ω is

$$\frac{F_0(k,L)}{\omega} = \frac{F_0(k,L)}{2Dk^2} = \frac{c_0 L}{2}\frac{1}{kL}\frac{\sinh(kL)}{\cos(kL) + \cosh(kL)}. \tag{3}$$

In the high- and low-frequency limits, Eq. (2) gives $\delta \to -\pi/4$ and $\delta \to -\pi/2$, respectively. The time dependence of the total number of atoms added to the surface is proportional to the integral of this flux. Thus, the total area A of the islands will be proportional to

$$A(t) \propto \int_0^t F(t')dt' \propto \frac{F_0}{\omega}\cos(\omega t - \delta - \pi/2). \tag{4}$$

So, in the low-frequency limit, where $\delta \to -\pi/2$, the area is in-phase with the temperature; for high frequencies, the area is out-of-phase by $\pi/4$. This is precisely what is observed in Fig. 6.

Since Eqs. (1)–(3) give expressions for the flux in terms of c_0 and D, measurements of the frequency dependence of the flux can be used to estimate the formation enthalpy and migration energy of the defects. To experimentally determine the flux, we marked the island step edges and then differentiated the numerically determined island area versus time and use the experimental observation that the flux is distributed among the steps according to their perimeter P, i.e.,

$$F \propto P(t)\frac{dA}{dt}. \tag{5}$$

To obtain δ, we fit the measured fluxes to Eq. (2).

Figure 7(a) shows the frequency dependence of the phase shifts δ measured at three temperatures. Despite some scatter at high temperature because of the difficulty in marking the

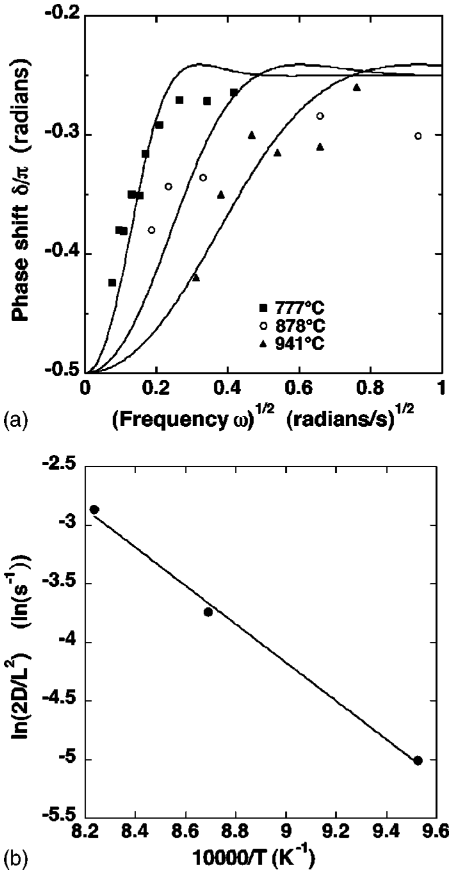

FIG. 7. (a) Plot of the dependence on frequency of the phase shift between the temperature oscillations and mass flux to the crystal surface for three different average temperatures. As the temperature increases, faster defect diffusion causes the phase shift to move toward the low-frequency limit. The lines are fits of experimental data (symbols) to Eq. (2) for the three temperatures. (b) Determination of the activation energy of defect migration from an Arrhenius plot of the temperature-dependent diffusion coefficients D determined in (a).

rapidly moving step edges, the 1D model adequately describes the experimental data. Moreover, the effect of temperature is clear—for a given frequency of temperature oscillation, increasing temperature moves the phase shift towards the low-frequency limit of $\delta=-\pi/2$. That is, the crystal equilibrates faster at higher temperature because the defect diffusion rate is higher.[69] Fitting the phase shifts to Eq. (2) gives $L^2/2D=149$, 42.3, and 17.6 s, respectively, for 777, 878, and 941 °C.

We note that Eq. (2) shows that the phase shift δ is a function only of the oscillation frequency and $L^2/2D$. Since D is independent of the concentration of thermal defects c_B, the phase shift is also independent of c_B. Physically, this independence occurs because the phase shift only depends upon the speed at which the defects diffuse (migrate), not upon their concentration. Since in our measurement method, D depends on temperature but not on the defect concentration, the defect migration energy E_M is directly determined by simply assuming that D depends exponentially on temperature with the activation energy being E_M. The Arrhenius plot in Fig. 7(b) then gives $E_M=1.41\pm0.09$ eV.

If we take L to be the crystal thickness (1.5 mm), an upper bound for D at 777 °C, calculated from $L^2/2D=149$ s, is 7.5×10^{-9} m^2/s. It is informative to crudely estimate the value of L in two other ways: First, from the self-diffusion coefficient measured from tracer diffusion measurements. Second, from the absolute amount of material that flows between the bulk and the surface during a temperature change and the estimated change in thermal defect concentration. Relevant to the first approach, Frank *et al.*[70] recently measured the self-diffusion coefficient of Ni at 1000 K in $Ni_{56.6}Al_{43.4}$ to be $D_{SD}\approx10^{-18}$ m^2/s. We emphasize that this diffusion coefficient includes the formation energy of the defect that mediates diffusion. In contrast, the D determined by our technique depends only upon the migration energy of the defect. Assuming that D_{SD} is proportional to the concentration of thermal defects, that is, $D_{SD}=c_BD$, we can deduce D from D_{SD} given the concentration of thermal defects. Including the contributions of lattice vibrations to defect entropy, Lozovoi and Mishin[62] have calculated that roughly one in 10^4 lattice sites in somewhat Ni-rich NiAl is a triple defect at 1000 K. Then $D_{SD}=10^{-4}\,D$ implies $D\approx10^{-14}$ m^2/s. Using this value for D and $L^2/2D=149$ s gives $L\approx1700$ nm. Alternatively, the distance L over which the thermal defects are transported between the surface and the bulk can be estimated from the experimentally observed mass flow that occurs during a temperature change and an estimate of the change in bulk defect concentration with temperature. Lozovoi and Mishin[62] calculate that the concentration of triple defects changes by about 10^{-3} per lattice site between 1250 and 1000 K. For roughly the same temperature change, we observe about five layers are transported between the surface and the bulk during cooling (see Fig. 3). If one in 10^3 sites of each layer is populated during cooling, then 5×10^3 layers must be communicating with the surface to remove five layers from the surface. Since the (110) planes in NiAl are separated by 0.2 nm, $L\approx5\times10^3\times0.2=1000$ nm. While crude, the two estimates are reasonably consistent and suggest that the surface serves as a source/sink for about the outermost several microns of the crystal. That is, the surfaces do not appear to be able to equilibrate the entire crystal. Internal sources/sinks, such as dislocations, must be present if the entire crystal is to equilibrate.

In addition to the migration energy of the thermal defects, we can determine the formation enthalpy (E_F) by measuring the flux to the surface as a function of temperature. In the case of Pt, this method reproduces the known result very well.[51] The bulk thermal defect concentration is expected to be proportional to $\exp(-E_F/kT)$. The concentration change Δc_B produced by a temperature change ΔT is then proportional to $\Delta T\exp(-E_F/kT)/T^2$. Since an island's area change is proportional to a Δc_B and [from Eq. (4)] is also proportional to F_0/ω, we have, in the limit of small frequencies,

$$\frac{\Delta c_B T^2}{\Delta T}=\frac{F_0T^2}{\omega\Delta T}\propto e^{-E_F/kT}, \tag{6}$$

which allows E_F to be determined from measurements of the flux amplitude F_0. We consider data for F_0 with frequencies small enough so that $\delta\leqslant-0.42\pi$.[71] Plotting $\ln(F_0T^2/\omega\Delta T)$

vs $1/T$ gives a line with $E_F = 0.64 \pm 0.07$ eV (see Fig. 3b of our brief report[47]). Statistical-mechanical analysis shows that the "effective" defect-formation enthalpy, E_F in Eq. (6), in Ni-rich NiAl is exactly one half the energy required to make the triple defect.[57–61,72] Our triple-defect formation enthalpy (1.28 eV) is somewhat lower than other less-direct experimental values for Ni-rich NiAl [1.65–1.83 eV (Ref. 73)] and considerably lower than that from theoretical calculations [2.0–2.4 eV (Refs. 57 and 59–61)]. The origin of this large discrepancy between theory and experiment is currently unclear, although we note that our crystal may be sufficiently far from stoichiometry as to invalidate some of the dilute-defect approximations used in theory.

If we assume that the diffusion rate of the triple defect is proportional both to an effective defect concentration and to the defect migration rate, the diffusion activation energy would be $E_F + E_M$ or $0.64 + 1.41 = 2.05$ eV. We next cautiously compare this activation energy with those determined by other experimental techniques. In our technique, both Ni and Al are diffusing, perhaps in a correlated manner, under a thermodynamic driving force imposed by the temperature change. Thus, we cannot compare directly to self-diffusion measurements, which determines the random walk of a single component without a driving force. We can compare, however, to the energetics of how fast a crystal equilibrates itself after a temperature change, as measured by electrical resistivity. For nearly stoichiometric NiAl, Ko *et al.*[74] and Kozubski *et al.*[75] measured activation energies of about 1.4 and 2.3 eV, respectively. Our value for the diffusion activation energy falls within this range, with the caution that electrical resistivity may be measuring a subtly different process than in our approach. Furthermore, interpreting these energies of crystal equilibration after a temperature change in terms of atomic processes is difficult. Consider the activation energies for Ni and Al diffusion in NiAl, which have been either measured or experimentally estimated. For $Ni_{56.6}Al_{43.4}$, Frank *et al.* measured the activation energy of Ni self diffusion to be 2.4 eV.[70] For the same alloy composition, Nakamura *et al.* have estimated the activation energy of Al self-diffusion to be considerably higher: 3.5–4.3 eV.[76] Because their diffusion energies are different, Nakamura *et al.* suggested that Ni and Al diffuse by different mechanisms.[76,77] In fact, at least five diffusion mechanisms[70,78,79] have been proposed for NiAl and no consensus exists as to which are operative for Ni and Al self-diffusion.[70,72,77] Furthermore, the activation energy for Ni self-diffusion decreases significantly as the composition becomes increasingly Ni-rich, suggesting that its diffusion mechanism changes with composition.[70,80] A measurement, using our approach, of the diffusion coefficient D as a function of stoichiometry would help resolve these issues.

To summarize this section, the temperature-change-driven mass transport between NiAl's surface and bulk is well described by a 1D model of bulk mass transport. By imaging the frequency-dependent response of nanoscale surface structure to temperature variations, we are able to measure the migration and formation energies of the bulk thermal defects. We suggest this technique may be useful for measuring properties of both surface and bulk diffusion processes. The 1D-diffusion model's success in simulating the phase shift and measuring the defect formation enthalpy provides strong evidence that the only large gradients in defect concentrations are perpendicular to the surface and that lateral gradients are small. If there are no lateral concentration gradients, there should be no mass transport through a subsurface current between *adjacent* steps of different curvature. That is, the rates of isothermal island decay should be largely independent of the local environment such as step density. We show that this is the case in the next section.

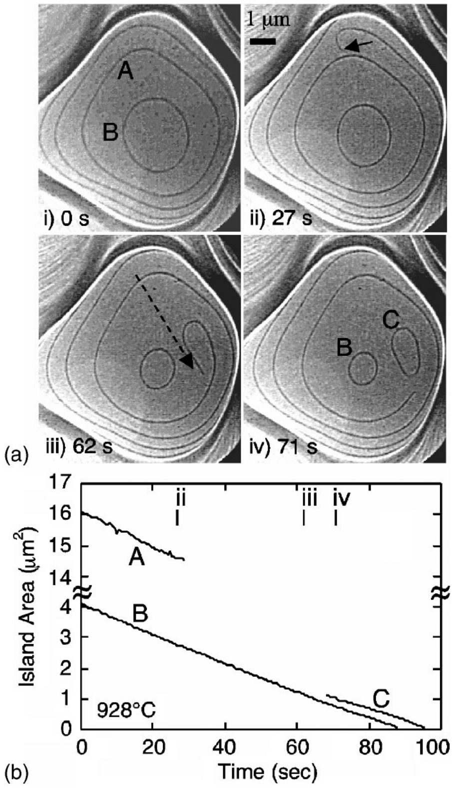

FIG. 8. (a) Low-energy electron micrographs captured during the constant-temperature decay of an island-stack structure on the NiAl (110) surface at 928 °C. The dark lines are the monoatomic surface steps. A dislocation with screw component meets the surface where the step ends [see arrow in image (ii)]. When the dislocation moves in the direction of the dashed arrow in image (iii), the step that emanates from it is extended, the closed step of island A is opened, and island C is formed. (b) Areas of the three labeled islands of part (a) versus time. The times at which the images of part (a) were captured are marked. Despite the large changes in the local step environment and even though the islands have different curvatures, the islands all decay at the same, constant rate. In addition, the larger island does not grow at the expense of the smaller island. That is, there is no coarsening of island size.

C. Surface smoothing

As it is extremely difficult to prepare perfectly flat crystalline surfaces, solid surfaces usually contain arrays of atomic steps. These step arrays are not in equilibrium because a surface can lower its free energy by decreasing the total step length. Figure 8 shows an example of this lack of stability on a NiAl (110) surface as observed at 928 °C. The

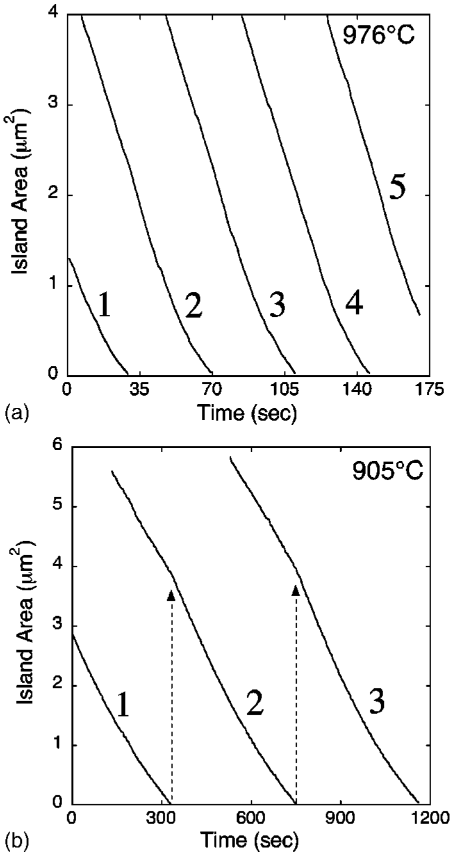

FIG. 9. Island areas as function of time as an island-stack structure evolves. The islands are numbered, starting at the top of the stack. In (a) at 976 °C when the topmost islands vanishes, there is essentially no change in the decay rate of the remaining islands. At 905 °C, (b), there is a small change in decay rate when the topmost island disappears, suggesting that diffusion between steps is just starting to affect the decay rate at this temperature.

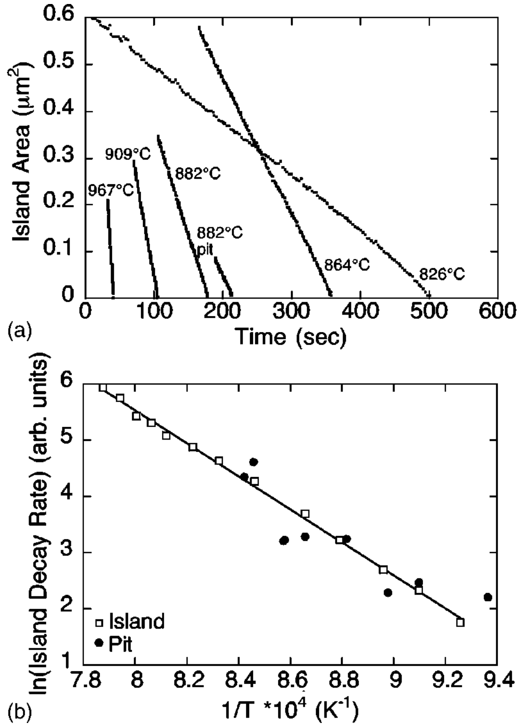

FIG. 10. (a) Island areas as a function of time for islands and pits on the NiAl (110) surface. (b) Arrhenius plot of the decay rates. An activation energy of 2.5±0.04 eV is found for the island rates.

surface consists of an island stack in a "wedding-cake" structure. Between 0 and ~30 s, the two topmost islands [islands A and B in the first two images of Fig. 8(a)] in the stack shrink. By reducing its step length, the surface lowers its free energy and, eventually, becomes smoother.

When smoothing occurs by surface diffusion, the consequences of mass transport between neighboring step edges are observable. As an island stack decays, mass leaves the topmost island as it shrinks. Since this mass current is on the surface, it must flow by the lower islands. Some of the mass diffusing away from the topmost island is captured by the lower islands.[19] These islands actually increase in size. This behavior is not observed for NiAl. Figure 9 plots the area of all islands in a stack that can be resolved at one time. Clearly, all the islands are shrinking; none are growing. Another consequence of the mass diffusing on the surface during smoothing is that an array of islands on the same terrace will "coarsen," that is, the larger islands grow as the smaller ones shrink.[22] We again emphasize that coarsening occurs because the mass leaving the smaller (less stable) islands flows on the surface. The larger islands capture some of this mass and grow. Image (iii) of Fig. 8(a) shows the formation of a second island (C) on the same terrace as island B due to the motion of a dislocation. Figure 8(b) (between about 70 and 90 s) shows that these two islands decay at the same rate, despite their differing size (curvature). That is, islands on the same NiAl terrace do not coarsen. Thus, we see neither of the two signatures of smoothing by surface diffusion for NiAl (110). Therefore, we come to the conclusion that mass is not being transported by surface diffusion.

Yet, during isothermal annealing, mass is being transferred from steps of positive curvature to steps of negative curvature. This fact is established in Fig. 10, which shows that pits fill in at the same rates as islands.[81] This observation establishes that sublimation is not significantly contributing to step motion, otherwise the pits would decay at a slower rate than the islands. Since mass is certainly flowing during smoothing and we see no evidence for surface mass currents, the only alternative is for the mass to flow through the bulk. In fact, island coarsening and the process of lower islands in a stack growing occur because of gradients in the concentrations of surface adspecies. These surface gradients and their observable consequences (e.g., island coarsening) are absent when the mass transport occurs primarily through the bulk. In the remainder of this paper, we further support the conclusion of smoothing via bulk diffusion and discuss its consequences.

Another remarkable characteristic of smoothing on NiAl is that all the islands shrink at nearly the same rate, regardless of the environment of each island, as seen in Fig. 9.[82] This independence of environment is clear from the complex sequence of events in the later panels of Fig. 8(a) where a bulk dislocation terminating at the surface moves through the field of view. The decay rates of the two topmost islands are

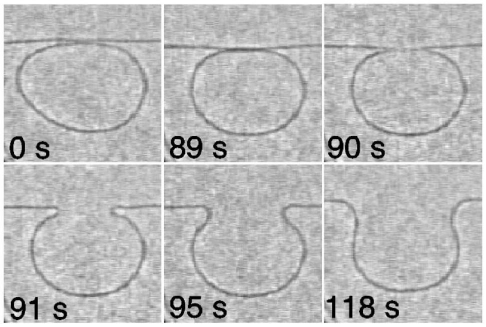

FIG. 11. Example showing that reduction of step curvature is a strong driving force for the NiAl (110) surface. The collision of a straight step with the closed step of a pit produces two steps that initially have highly curved sections. In only a few seconds at 784 °C, the highly curved sections reduce their length and straighten greatly, establishing that step curvature is a driving force for step motion. Images are $1.3 \times 1.3\ \mu\text{m}^2$.

unperturbed despite the large changes in local environment resulting from the dislocation motion. Furthermore, when the topmost island of an island stack and thus the emitted current vanishes, the decay rate of the remaining islands is largely unchanged [see Fig. 9(a)]. As illustrated in Fig. 10, with the exception of the lowest temperature examined, we find that both islands and pits shrink at a constant rate when they are sufficiently small.[83] We next show that the linear decay kinetics and the independence of the smoothing kinetics on environment are consequences of the relative energies of the different processes involved in smoothing.

We begin by developing a simple analytic description of smoothing kinetics mediated by bulk diffusion.[84] To do this, we need to describe the chemical potential of steps, which is generally expressed as a function of the step curvature using the Gibbs-Thomson relationship. That is, the greater the curvature, the greater the chemical potential, and the greater the driving force to reduce step length. Figure 11 shows that this behavior is also valid for NiAl (110)—two “hairpin” sections of step are created by the collision of a step and a pit. The highly curved hairpin sections accrete mass and rapidly become straighter by reducing their length. This is exactly the behavior expected for curvature-driven step motion. Then, based on the success of the 1D model of bulk diffusion proposed above, we assume that each step edge interacts with the same uniform reservoir of bulk defects. The smoothing should then follow the same kinetics as if steps were exchanging atoms with a uniform vapor phase.[85] In this situation the flux of atoms F to each segment of step edge will be equal to

$$F = \frac{\Gamma}{kT}(\mu_{reservoir} - \mu_{island}), \tag{7}$$

where Γ is the step mobility and $\mu_{reservoir}$ and μ_{island} are the chemical potentials of atoms in the bulk and islands, respectively. The rate of change of each island’s area will be this flux multiplied by the island perimeter. From the Gibbs-Thomson equation, $\mu_{reservoir} - \mu_{island} \propto c_0\beta/R$ where β is the step free energy per unit length, c_0 is the bulk equilibrium defect concentration, and R is the radius. Thus,

$$\frac{dA}{dt} \propto c_0 \frac{\beta\Gamma}{kT}.$$

That is, an island shrinks at a constant, time-independent rate.

We emphasize that the observed kinetics establish that the isothermal smoothing of the NiAl (110) surface, at sufficiently high temperature, is not controlled by the *rate* of bulk transport. Instead, smoothing is controlled by the rate at which bulk defects exchange near steps, i.e., the step mobility. That is, the step mobility is proportional to the probability that an atom or vacancy next to the step edge will attach to the step edge. Our results thus imply that the energetic barrier for bulk/surface exchange is large compared to the barrier to diffusion in the bulk.[86] Indeed, the energies we have measured are consistent with this interpretation. The rates of island decay exhibit Arrhenius behavior with an activation energy of 2.54 ± 0.04 eV (see Fig. 10). Since the defect formation enthalpy is 0.64 eV, the rate of bulk/surface-step defect exchange Γ has an activation energy of 1.9 eV. The exchange near surface steps is slow compared to bulk diffusion because this energy is higher than the energies required to thermally generate (0.64 eV) and move (about 1.4 eV) defects.

The fact that bulk/surface exchange is slow compared to bulk diffusion accounts for the relative independence of the smoothing rates on the local environment, such as its step density. Then any (nanoscale) gradients parallel to the surface caused by defect emission from step edges is quickly eliminated by fast defect diffusion. As a consequence, adjacent surface features of different curvature cannot transfer mass through a near-surface current because there are no substantial lateral gradients between neighboring steps. We emphasize that the kinetics of smoothing dominated by bulk diffusion do not have to be independent of the local environment. NiAl is a special case—the environment-independent kinetics occurs because the attachment/detachment step is difficult relative to bulk diffusion.

As the temperature is lowered, however, diffusion between neighboring steps is beginning to affect the decay kinetics, as illustrated in Fig. 9. At 976 °C [Fig. 9(a)], there is essentially no change in the decay rate of the stack’s second island as the topmost island vanishes. At 906 °C [Fig. 9(b)], however, there is a small but noticeable change in decay rate when the topmost island vanishes. It is possible that this very small effect is a sign that the attachment barrier is becoming less important at lower temperature. Another possibility is that currents due to surface diffusion are just becoming significant.

In principle, the environmental independence of island decay could be explained by surface diffusion alone if there were a large adatom attachment barrier and if the steps were highly permeable, i.e., if adatoms or advacancies on approaching a step were much more likely to diffuse over them than to attach to them.[28] This alternative explanation seems unlikely. Even in 10-μm-wide regions of the surface, we see no evidence for surface mass conservation during smoothing.

If the mass current was confined to the surface, then, the Ni and Al atoms must cross over many steps before being captured. That is, the permeability and attachment barrier would have to be extremely large. Yet such a large attachment barrier has no obvious atomic origin— Ni and Al adatoms should bind easily to step edges. It thus seems much more likely that bulk-surface exchange—a process that is in abundant evidence—is responsible for the observed island decay.

To summarize this section, the NiAl (110) surface smoothes by transporting mass between a uniform bulk reservoir and surface steps. This causes material to be subtracted from positively curved steps (i.e., islands) and added to negatively curved steps (i.e., pits). This mass transport occurs by diffusion through the bulk. Because the exchange of bulk defects with surface steps is difficult relative to making and transporting bulk defects, the concentration of bulk defects is relatively uniform laterally. The combination of attachment/detachment-limited kinetics and mass transport through the bulk accounts for the observation that islands (and pits) decay with linear kinetics with rates that are nearly independent of the local step density.

IV. CONCLUSIONS

In this work we have shown that by monitoring the motion of surface steps as a function of temperature, basic information about bulk defects and their creation at a surface can be obtained. For NiAl we find that the bulk thermal defects are created and destroyed near step edges. A natural question is “how general is this result?” The answer clearly depends on how fast surface diffusion is.

In perhaps the simplest scenario, whether a bulk thermal defect (e.g., a vacancy) can be annihilated on a terrace will depend on the existence of diffusing thermal adatoms. The ultimate source of these adatoms is step edges. If the diffusion rate of the adatoms is relatively slow compared to their annihilation rate by bulk defects, i.e., if their diffusion length is small, the effect will be that bulk defects will only be destroyed near step edges, as we observe for NiAl. The fact that we find that surface diffusion has a negligible effect on NiAl’s surface smoothing is consistent with this scenario.

In the classical theories of surface smoothing by bulk diffusion, Mullins assumed that the surface is a uniform and perfect sink/source of vacancies.[4] However, our work on NiAl shows that most of the surface, i.e., the terraces, is not a good source of thermal defects (vacancies). Instead, the only effective sources are the surface steps. Therefore, the ability of a surface to be a source/sink can depend on the local step density. Thus, just as the continuum theory of Mullins provides an incomplete description of smoothing mediated by surface transport when step processes are important,[87] the theory will not completely describe surface smoothing mediated by bulk transport.

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[82] The decay rates of noncircular islands generally decrease somewhat as the islands shrink. We believe that this effect results from anisotropy in the step velocity as a function of step orientation. In contrast, if islands remain nearly circular, their decay rates remain linear [see Figs. 5(b) and 8].

[83] As the island vanishes at the lowest temperature in Fig. 10(a), its area decreases nonlinearly, suggesting that diffusion is becoming important.

[84] We note that during isothermal surface smoothing only the surface is out of equilibrium. In contrast, after a temperature change, the entire sample is not equilibrated. How fast the bulk then equilibrates is controlled by the rate defects diffuse through the bulk, as described by the diffusion model.

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to the oscillations and will be time independent. The flux is then determined by the time-dependent state of the surface: $F \propto \cos(\omega t)$. Therefore, the phase shift δ between the temperature and the flux will be essentially zero, much smaller then the $-\pi/4$ limit of Eq. (2). As the frequency decreases, the concentration near the surface has time to come into equilibrium with the surface and the analysis of Eqs. (1)–(4) becomes correct. The fact that the smallest phase shift we observe is $-\pi/4$, not zero, indicates that we are in the frequency regime where the step-attachment barrier is not important to temperature-change-driven mass flow between the bulk and the surface.

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