



Directly Observing the Surface Dynamics of an Engineering Alloy

Vacancies are good things when you're on vacation and don't have reservations. In materials, they also enable a bit of flexibility. Atoms can occupy empty spaces in a crystal lattice much like baseball fans in the bleachers can switch to seats in the shade as the sun moves. A Sandia research team has observed that the generation and annihilation of vacancies in an alloy allow the alloy surface to smooth and roughen with changing temperature -- confirming a 50-year-old hypothesis and contravening the current conventional wisdom. Their findings can help direct fabrication of nanodevices and may explain other processes, like rusting.

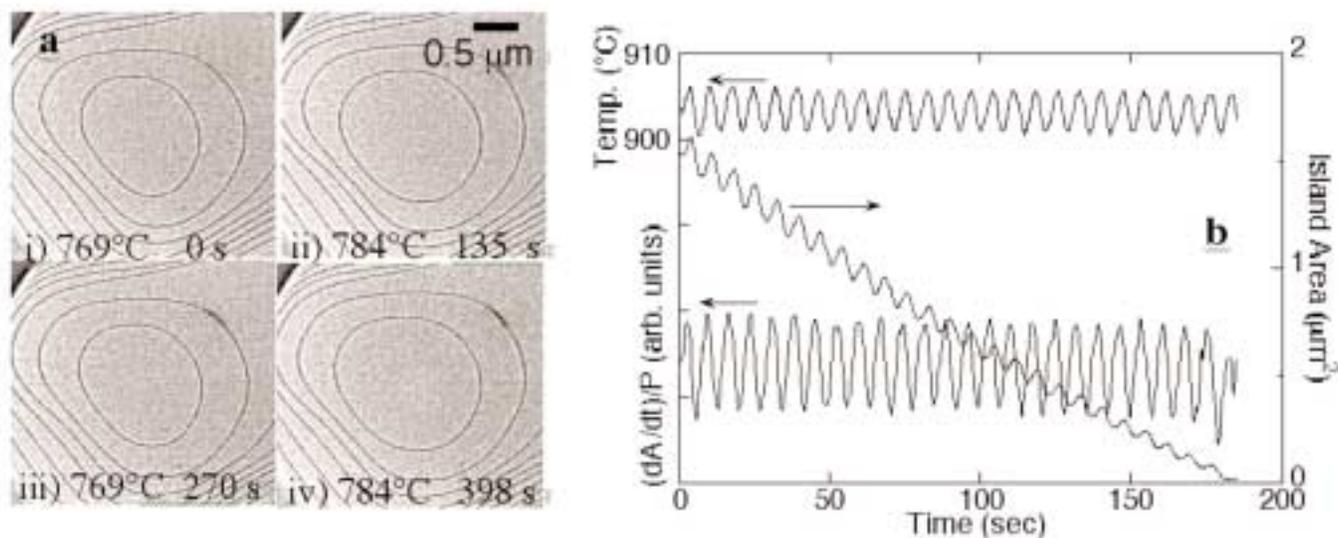
Motivation and Approach

Currently, science cannot predict with sufficient accuracy the performance and reliability of real engineering materials. Traditionally, the approach of materials science to develop this predictive capability has emphasized "forensic" analysis, where a material is

analyzed after being processed or functioned.

Unfortunately, this approach frequently leads to ambiguity about the nature of the underlying physical processes. For example, how a surface's morphology smooths and where defects (vacancies) form in a solid are not well known even though these processes control the ability to fabricate engineered materials and nanoscale features.

A more powerful approach, which is enabled by new experimental techniques, is to directly observe how materials respond during processing or use. In this manner, the dominant processes can be directly identified and their rates quantified. Here we have used low-energy electron microscopy (LEEM) to study what happens on the surface of the intermetallic alloy NiAl as it is heated or cooled. This material is the model for lightweight alloys suitable for high-temperature, high-strength applications such as turbines. LEEM images the steps on a crystalline surface



a) LEEM micrographs of an island-stack structure on the NiAl (110) surface as the temperature is varied about a mean of 776 °C. The dark lines mark the atom-high surface steps. With increasing temperature, bulk atoms come to the surface since the concentration of thermal vacancies in the bulk increases. For decreasing temperature, the islands shrink in size because material leaves the surface to reduce the bulk vacancy concentration. b) Island area $A(t)$ and the rate of change normalized by the perimeter $(dA/dt)/P$ as the temperature is sinusoidally oscillated by about ± 2.5 °C around a mean of 903°C. Even though the island area decreases greatly because of thermal smoothing, the area change resulting from the temperature oscillation scales exactly as the perimeter of the island.



and by watching their motion in real time, the dynamics of mass transport can be directly followed.

A multidisciplinary team was required to perform this work. The effort consisted of experimental observations (Kevin McCarty), theory and modeling (Norman Bartelt), and sophisticated, automated image analysis (Jan Nobel). The latter required the development of new algorithms and programs to track the position of image features (surface steps) as a function of time.

Accomplishment

We measured the thermal smoothing of a NiAl surface by directly observing step motion in real time. Islands, with their curved steps, are thermodynamically unstable with respect to straight steps just as small liquid drops are unstable compared to a flat surface (the Gibbs-Thomsen effect).

Because of this, the system can lower its energy by transferring mass from highly curved steps to steps of lower curvature. In this manner, the surface “smooths” and becomes flatter. Remarkably, the decay rates of all islands in a stack are constant in time and totally independent of the local environment (e.g., the width of the immediately adjacent terraces). Given the lack of any surface current between islands of different curvature, we know that surface diffusion is not important to the smoothing process. Instead, we

find striking evidence that bulk vacancies are responsible — we directly observe exchange between bulk vacancies and the surface when the sample’s temperature is changed.

As shown in the figure, we oscillate the sample’s temperature and observe the response of the nanoscale surface structure as a function of frequency (a version of Ångström’s method of measuring thermal conductivity). We find that vacancies are generated (and annihilated), not over the entire surface, but only near atomic steps.

Significance

Our finding that surface smoothing can be dominated by transport through the bulk confirms the mechanism proposed nearly fifty years ago by Herring and Mullins. However, current conventional wisdom is that surface diffusion dominates surface smoothing. We expect similar behavior will be directly observed in other alloys and elemental metals. That vacancies on the NiAl surface are generated and annihilated only near the step edges undoubtedly affects how other processes involving vacancies (e.g., surface oxidation) actually occur. We have also demonstrated a new and powerful way to measure important properties of bulk materials such as defect migration and formation energies.



KEVIN McCARTY (lower right) earned his PhD at Iowa State University and has been a Sandia staff member since 1985. JAN NOBEL (middle) has been a Sandia staff member since 1998 and earned his PhD at the University of Maryland, as did NORMAN BARTELT (left), who has been a Sandia staff member since 1997.