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FILED ION MICROSCOPY AND ATOM-PROBE MASS SPECTROSCOPY:
TECHNIQUES AND SELECTED APPLICATIONS

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Abstract

The techniques of field ion microscopy and atom-probe mass spectroscopy are reviewed with emphasis on the general operational principles of the instruments and selected applications in the area of surface science. The single atom imaging capability of the field ion microscope is shown to make it uniquely suited to the study of detailed, atomic processes on clean metal surfaces. As examples, investigations of single-atom surface diffusion, cluster nucleation, and surface reconstructions are discussed. The ability of the atom-probe mass spectrometer to determine the chemical identity of selected atoms observed in the field ion microscope image is shown to be useful for the microanalysis of various materials. The different types of atom-probes currently in use and their application in the areas of surface catalyzed reactions and high-temperature ceramic superconductors are described.

Introduction

The atom-probe field ion microscope is a unique microanalytical instrument which is used to investigate the structure and composition of solid materials on an atomic scale. The instrument combines a field ion microscope (Müller, 1951), which provides an atomic-resolution image of solid surfaces, with an atom-sensitive time-of-flight mass spectrometer or "atom-probe" (Müller et al., 1968). By itself, the field ion microscope is well-suited to investigate phenomena such as single-atom surface diffusion, atom interactions and cluster formation, surface reconstructions, and formation of various defect structures. When used in combination with the atom-probe, the instrument has made unique contributions in areas such as surface segregation, surface chemical reactions, semiconductor-metal interface phenomena, and a wide variety of metallurgical problems. In this paper a brief review of the field ion microscope and atom-probe techniques is presented. More recent developments such as the imaging and pulsed-laser atom-probe are emphasized. Also included in the review are selected applications of the field ion microscope and atom-probe which point out some of the unique aspects of the techniques. These applications are drawn primarily from research conducted in the author's laboratory.

Field Ion Microscopy

Unlike conventional surface analytical techniques, the field ion microscope relies on extremely high electric fields to probe the atomic structure of solid surfaces. To produce these high electric fields at reasonable applied voltages, the sample must take the form of a sharply-pointed needle (commonly called a "tip") with a radius of curvature at the apex of the order of several tens of nanometers. In field ion microscopy a direct image of the atoms at the apex of the tip is obtained by the application of a high positive voltage to the tip in the presence of an imaging gas (usually an inert gas such as He or Ne). The electric field at the apex, which is of the order of several tenths of a volt/nm, causes the imaging gas atoms above the surface to become ionized. Once formed, the ions are projected away from the tip surface by the electric field to a fluorescent screen. The pattern of spots formed by these "field ions" is a direct image of the protruding surface atoms. The images consist of both flat, single-crystal planes, which appear as dark areas, and

Key Words: Field ion microscope, atom-probe, imaging atom-probe, pulsed-laser atom-probe, surface diffusion, cluster nucleation, surface reconstruction, surface chemical reaction, catalysis, high-temperature superconductors.

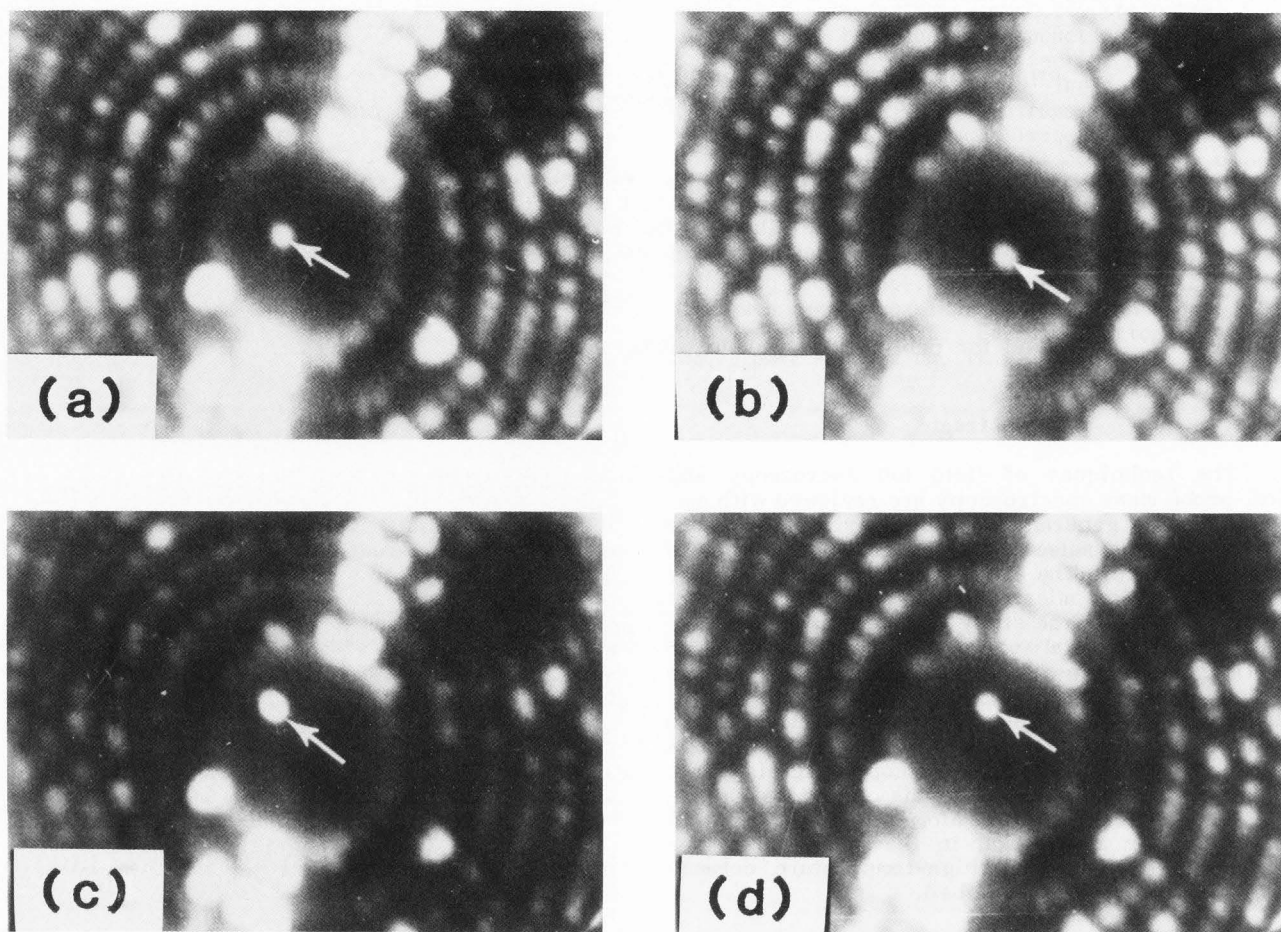


Fig. 1. A series of field ion microscope images showing the diffusion of a single Ni atom on the W(110) plane. Between photographs the sample tip was warmed from a temperature of 77 K to 200 K for one minute. (Kellogg, 1987c)

atomically stepped regions which appear as concentric rings of spots.

At applied voltages typically a little higher than those required for ion image formation, it is possible to remove the surface atoms themselves. This process, known as field evaporation or field desorption, removes surface atoms one atomic layer at a time. Field evaporation is routinely used to produce atomically smooth and clean surfaces, and, as discussed later, it is the process which underlies the operation of the atom-probe mass spectrometer.

One of the most unique applications of the field ion microscope is the investigation of the diffusion of individual surface atoms (Ehrlich and Hudda, 1966). In a typical surface diffusion experiment, a single atom is deposited on a flat single-crystal plane where it forms a high contrast image spot on a dark background. At the cryogenic temperatures used for imaging, the atom is immobile. Motion is induced by warming the tip with the applied voltage turned off. After a given time interval, the tip is re-cooled to cryogenic temperatures and the atom is frozen in place. A second field ion image is obtained which shows the new position of the atom. The displacement of the atoms is determined from superposition

of the two images. This process is repeated tens to hundreds of times at a given temperature and the mean square displacement of the atom is determined. As an example, Fig. 1 shows a series of field ion micrographs in which the displacements of a Ni atom on W(110) at a temperature of 200 K are observed (Kellogg, 1987c). From the temperature dependence of the mean square displacement, quantitative diffusion parameters are obtained. This technique has been used to obtain the activation energy of surface diffusion for a variety of metal-adsorbate/metal-substrate systems (Kellogg et al., 1978; Tsong and Cowan, 1978; Ehrlich and Stolt, 1980; Bassett, 1983). More recently, the diffusion of non-metallic adsorbates such as silicon (Tsong and Cassanova, 1981) and sulfur (Kellogg, 1985a) have been investigated with this technique.

The clustering of individual surface atoms can also be examined in the field ion microscope. In these experiments two or more atoms are deposited randomly on a single crystal surface. The tip is warmed and the atoms migrate on the surface until they encounter each other. Field ion microscope images reveal the type of clusters which are formed. By examining the distribution of sites occupied by

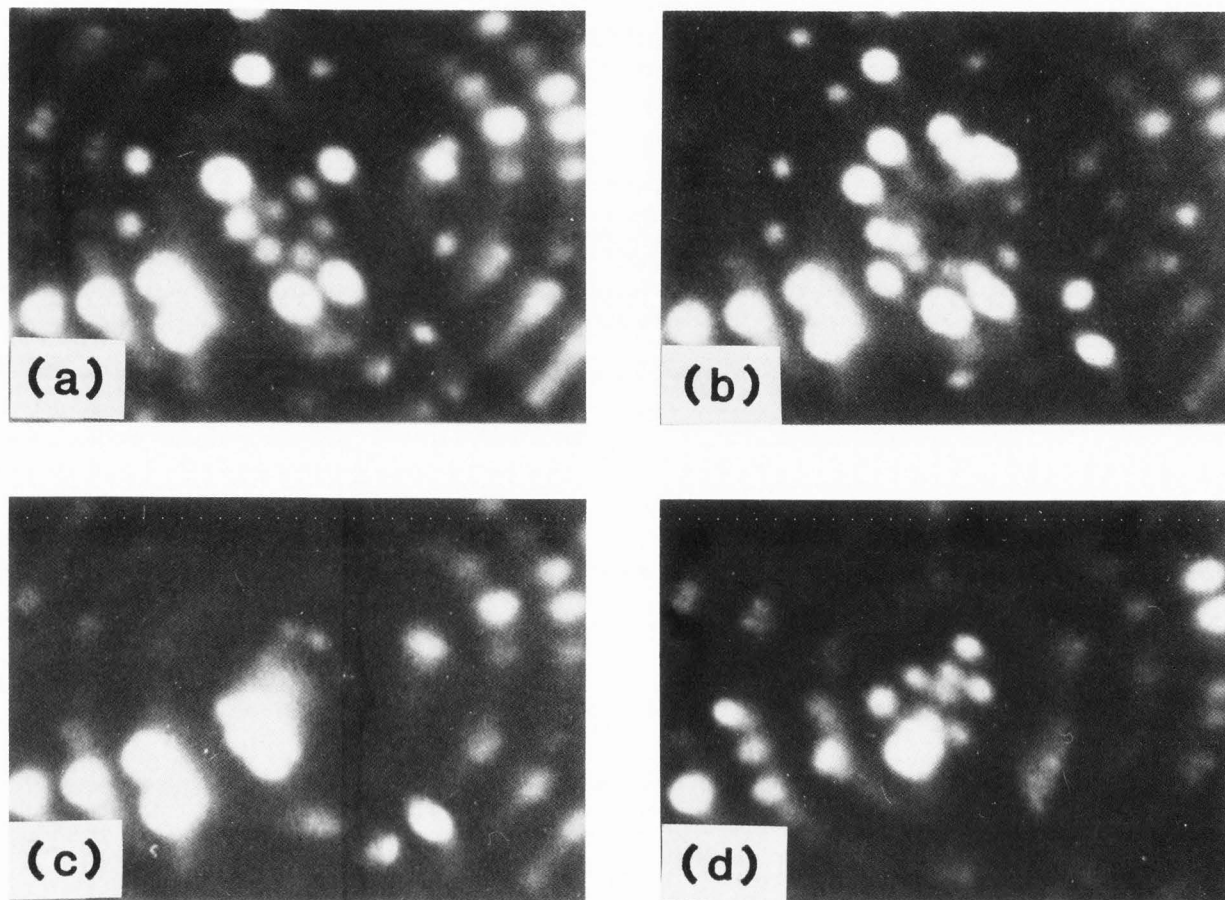


Fig. 2. A series of field ion microscope images showing the formation of a Pt-Pd mixed-metal cluster on W(110). (a) Ten Pt atoms were deposited at 77 K. (b) Approximately ten Pd atoms were added at 77 K. (c) After heating to 275 K a two-dimensional cluster was formed. (d) The Pd atoms were field evaporated leaving the original ten Pt atoms. Ordering within the cluster was not detected.

two diffusing atoms it is possible to measure their interatomic potential as a function of separation (Cassanova and Tsong, 1980, and references therein). Moreover, by depositing more than two atoms, one can determine how clusters nucleate and grow on a perfectly defined surface. Interestingly, for certain atoms the clusters nucleate as one-dimensional chains, whereas for others the nucleus is a two-dimensional cluster (Bassett, 1978; Fink and Ehrlich, 1981; Bassett, 1983; Schwoebel and Kellogg, 1988).

Recent investigations in the author's laboratory have been concerned with the formation of mixed-metal clusters. The purpose of these experiments is to determine if two different types of metal atoms on a third different metal substrate will uniformly mix and, if so, whether or not the mixed cluster will be ordered. Initial investigations have focused on mixed clusters of Pt and Pd atoms on the (110) surface of W (Schwoebel and Kellogg, to be published). This system was chosen because Pd and Pt atoms migrate at similar temperatures on W(110), but have significantly different evaporation fields. It is thus possible to distinguish between the two types of atoms in a cluster by removing the Pd at field strengths which leave the Pt atoms unperturbed.

The procedure used in the study of mixed-metal

clusters is illustrated by the series of field ion micrographs shown in Fig. 2. Fig. 2(a) shows ten Pt atoms on the topmost (110) plane of W. These atoms were deposited at 77 K and are immobile during imaging. Atoms near the edge of the plane produce larger image spots because of the higher electric field in these regions. Fig. 2(b) shows the same surface after approximately ten Pd atoms have been added. The surface was then heated to a temperature of 275 K. During this heating interval the deposited atoms formed a single, two-dimensional cluster as shown in Fig. 2(c). The applied voltage was then raised to field evaporate the Pd atoms. The new positions of the ten original Pt atoms are shown in Fig. 2(d). The large diffuse spot in Fig. 2(c) indicates that the atoms do mix to form a single cluster, and from Fig. 2(d) it is clear that the Pt atoms in the mixed cluster are not ordered. This result is consistent with the fact that Pt and Pd do not form ordered three-dimensional alloys. Additional experiments are being performed to examine the temperature dependence of the two-dimensional alloy formation.

Another unique application of the field ion microscope involves surface reconstruction. It is well known from Low Energy Electron Diffraction (LEED)

and other techniques that the atomic structure of a solid surface is often different from a simple termination of the bulk structure. The details of the atomic rearrangement, however, are sometimes difficult to obtain from diffraction techniques. An example is the (110) surfaces of Pt, Ir, and Au. The reconstruction of these 5-d fcc(110) surfaces is characterized by a (1x2) LEED pattern, which implies that the surface atoms have the same spacing as the bulk atoms in a direction parallel to the close-packed $[1\bar{1}0]$ rows, but twice the spacing in a direction perpendicular to these rows. In the particular case of Pt, there has been some controversy as to the atomic structure giving rise to this (1x2) diffraction pattern. Investigations with the field ion microscope have shown unambiguously that the (1x2) reconstruction of Pt(110) is due to alternate missing rows of atoms in the $[1\bar{1}0]$ direction (Kellogg, 1985b).

The reconstruction of Pt(110) from the unreconstructed (1x1) surface to the reconstructed (1x2) surface is shown in Fig. 3. Fig. 3(a) shows a field ion microscope image of a field-evaporated Pt surface in the vicinity of the (110) plane. The topmost (110) plane consists of four short chains of atoms and a single atom lying in adjacent channels of the underlying surface. The ability to produce atomically perfect, unreconstructed surfaces by low-temperature field evaporation is an especially useful feature of the field ion microscope for the investigation of surface reconstructions. Fig. 3(b) shows an image of the same surface after it had been heated to 330 K for one minute. During the heating interval the applied field was turned off. It is clear from Fig. 3(b) that the topmost atoms of the (110) plane rearranged during the heating interval. Careful analysis of the field ion image along with slow field evaporation indicated that the rows of atoms in Fig. 3(b) are in every other channel of the underlying surface, i.e., a missing-row structure. In other experiments it was shown that this missing-row structure could be produced for as few as five atoms on the surface indicating that the reconstruction is driven by short-ranged atomic interactions.

In more recent investigations these same procedures have been applied successfully to the reconstruction of other surfaces of Pt and Ir (Gao and Tsong, 1986; Witt and Miller, 1986; Kellogg, 1986; Tsong and Gao, 1987; Kellogg, 1987a, Gao and Tsong, 1987). In some of these investigations it has been shown that the processes involved in surface reconstructions can be followed in atomic detail if pulsed-laser heating is used to stimulate the atomic rearrangements (Gao and Tsong, 1986; Tsong and Gao, 1987; Gao and Tsong, 1987). Field ion microscope investigations of surface reconstructions have not been restricted to metals, unique reconstructions on some of the higher index surfaces of Si have also been identified (Liu et al., 1987). In even more recent work, reconstructions induced by adsorbates have been examined by field ion microscopy (Kellogg, 1988).

The above discussion provides just three examples of unique applications of the field ion microscope related to the area of surface science. Many other applications, particularly in the areas of metallurgy and materials science, have been reported and are reviewed in the literature (Müller and Tsong, 1969; Bowkett and Smith, 1970; Brenner, 1978; Panitz, 1982).

The field ion microscope is primarily a probe of surface structure. It is possible to obtain information related to the composition of the sample surface and near-surface region with an extension of the field ion microscope known as the atom-probe mass spectrometer. There are several types of atom-probes currently in use. In this section a brief description of the different types of atom-probes will be given and two selected applications will be discussed.

The most widely-used atom-probe follows the original design developed by Müller et al. (1968). In this instrument a small probe-hole is placed in the viewing screen of a field ion microscope. The image is adjusted such that the atom or atoms of interest are in alignment with the probe hole. Surface atoms are removed from the sample tip as positive ions by the application of a short-duration, high-voltage electrical pulse. The ions of interest travel through the probe hole and enter a drift tube. The mass-to-charge ratios of the ions are determined from a measurement of their flight time through the drift tube. The ability to identify particular atoms which may be associated with structural defects observed in the field ion microscope image makes this type of atom-probe particularly well suited for investigation of metallurgical problems (Brenner, 1978; Ralph et al., 1982; Smith, 1986; Miller, 1987).

The type of atom-probe used in the author's laboratory is known as the imaging atom-probe (Panitz, 1978). In this instrument the field ion microscope screen is replaced with an imaging detector which is sensitive to the impact of individual ions. For each ion which strikes the detector both a current pulse and a transient image spot are produced. Surface species desorbed from anywhere on the imaged portion of the surface are detected and identified by their flight times. This increased signal makes the imaging atom-probe better suited to the investigation of surface adsorption and reaction processes. However, the shorter flight paths used in the imaging atom-probe results in significantly poorer mass resolution.

The imaging atom-probe can also be used to obtain elemental maps of selected species by time gating the detector (Panitz, 1978). The detector gain is first reduced to a level at which no image spots appear. A desorption pulse is applied which removes surface atoms as positive ions. At a specified time later, a gate pulse is supplied to the detector over a time interval when the ion or ions of interest arrive. The detector displays a transient pattern of spots which is due to only the species of interest. This pattern is compared to a field ion image to determine where on the surface the species of interest was located.

An example of how the time-gated, imaging atom-probe is used is shown in Fig. 4 (Brenner and Kellogg, unpublished). Fig. 4(a) is a neon field ion micrograph taken from an Fe-3at.% Mo alloy nitrided for 14 days at 480 C in an 11% NH_3/N_2 mixture. Brightly imaging bands are clearly seen. Atom-probe mass spectra taken from this sample contained signals corresponding to the Fe matrix as well as Mo and MoN. Fig. 4(b) shows a time-gated image in which the gate was set for ions of Mo^{++} and MoN^{++} and Fig. 4(c) shows a time-gated image in which the gate was set for Fe^{++} ions. The enhancement of Mo

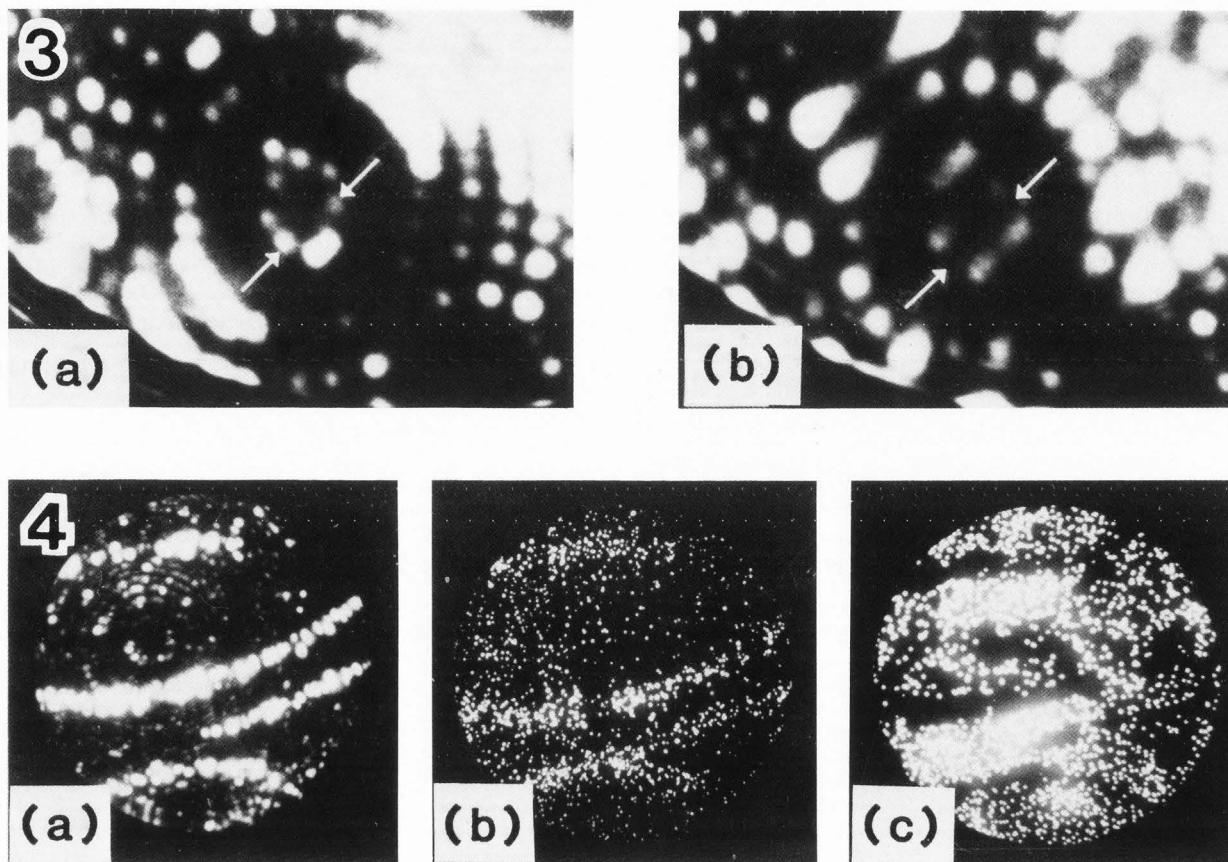


Fig. 3 (top). Field ion micrographs showing the reconstruction of a Pt(110) surface from a bulk terminated structure to a missing-row structure. Between the photographs the sample was heated to 330 K for one minute. The small arrows point to a row of atoms in (a) that is missing in (b). (Kellogg, 1985b).

Fig. 4 (bottom). (a) A field ion microscope image from an Fe-3 at.% Mo alloy nitrided in a NH_3/N_2 mixture. (b) A time-gated, imaging atom-probe micrograph from the same surface in which the gate was set to image Mo^{++} and MoN^{++} ions. (c) A time-gated, imaging atom-probe micrograph from the same surface in which the gate was set to image Fe^{++} ions. The brightly imaging bands in (a) are MoN precipitates. (Kellogg and Brenner, unpublished).

and MoN ions and the absence of Fe ions from the brightly imaging regions confirm previous studies with a probe-hole indicating that these regions are due to MoN precipitates (Brenner and Goodman, 1971). Thus, the spatial distribution of precipitate phases in alloys can be directly observed in the imaging atom-probe. Other applications of the time-gated imaging atom-probe can be found in the literature (Panitz, 1978).

Atom-probe investigations of semiconductors and insulators have been greatly facilitated with the development of the pulsed-laser atom-probe (Kellogg and Tsong, 1980). In this instrument the high-voltage electrical pulse used in the conventional atom-probe is replaced with a dc voltage and a short-duration laser pulse. Time-of-flight mass analysis is performed as in the conventional probe hole or imaging atom-probe. The elimination of the high-voltage pulse not only permits analysis of high resistivity materials, but also is useful for the investigation of surface chemical reactions and a variety of field desorption phenomena. A review of the pulsed-laser atom-probe technique has been published recently

(Kellogg, 1987b).

As in the case of the field ion microscope, the major application of the atom-probe has been in the area of metallurgy (Brenner, 1978; Ralph et al., 1982; Smith, 1986; Miller, 1987). However, in this review only two applications related to surface and materials science will be described. The first involves surface chemical reactions and the results have direct implications in the area of heterogeneous catalysis. The second is concerned with the microscopic properties of the new high-temperature, ceramic superconductors.

The reaction which was investigated was the CO oxidation reaction on Rh (Kellogg, 1985c). This reaction is obviously very important in the control of automotive exhausts as Rh is used in commercial three-way catalytic converters. It was discovered in previous studies that the CO oxidation rate on Rh dispersed-particle catalysts and single crystals first increases as the oxygen partial pressure is increased and then decreases at higher oxygen partial pressures (Oh and Carpenter, 1983; Peden et al., 1988). At 500 K the decrease in reaction rate or "deactivation"

occurred at an O_2/CO ratio between 30/1 and 40/1. The specific goal of the atom-probe investigation was to determine the surface process responsible for this deactivation. The atom-probe field ion microscope is particularly attractive for this type of study because the analyzed surface of a field ion tip is a good model of a catalyst particle.

In order to carry out the reaction at the required total pressures, an apparatus was constructed in which the sample could be heated in the reactant gases at pressures up to an atmosphere and then transferred under ultrahigh vacuum to an imaging atom-probe without exposure to air. The experimental procedure consisted of preparing the tip in the atom-probe by field evaporation, transferring the tip to the reaction chamber, heating the tip to 500 K in various mixtures of O_2 and CO at total pressures between 1 and 2 Torr, transferring the tip back to the atom-probe, and analyzing the surface and near surface composition. In Fig. 5 representative mass spectra recorded at O_2/CO ratios of 30/1 and 40/1 are shown. It was discovered from the atom-probe analysis that at ratios of 30/1 or less the surface composition was primarily CO and surface carbon, whereas at ratios of 40/1 or greater a surface oxide was present. A detailed analysis of the atom-probe data indicated that the oxide formed at the higher O_2/CO ratios was stoichiometric Rh_2O_3 (Kellogg, 1985c). The direct correlation between the conditions where the oxide formed and the deactivation of the reaction provided conclusive evidence that the deactivation was induced by the formation of the surface oxide. Moreover, atom-probe analysis made it possible to identify the chemical composition of the oxide.

In the investigation reported above, the reaction and analysis were carried out separately in order to determine the effect of the reaction on the surface at relatively high partial pressures of the reactant gases. The atom-probe has also been used to investigate surface chemical reactions as they proceed. In these studies it is possible to identify reaction intermediates and examine their crystallographic specificity. Examples of such "low-pressure" studies with the atom-probe include the formation of various metal carbonyls and the ammonia synthesis reaction. These types of studies are reviewed in an article by Block et al. (1986).

Investigations of high-temperature, ceramic superconductors with the atom-probe have been conducted to determine variations in their structure and composition on an atomic scale. Despite the intensive research devoted to these materials, considerable uncertainty still exists about their structural and chemical homogeneity. As a result, initial investigations have been conducted in several laboratories to determine the feasibility of field ion microscope and atom-probe analysis of the ceramic superconductor $YBa_2Cu_3O_{7-x}$ (Kellogg and Brenner, 1987; Melmed et al., 1988; Nishikawa and Nagai, 1988; Cerezo et al., 1988).

In our investigations (Kellogg and Brenner, 1987) field ion microscope tips were prepared from rods of hot-pressed $YBa_2Cu_3O_{7-x}$ by conventional electropolishing procedures. Atomic-resolution field ion microscope images of these tips were obtained with hydrogen as the imaging gas. Fig. 6 shows a hydrogen field ion image taken from one of the samples. The rings of spots are the edge atoms of

individual atomic or multi-atomic layers. Computer simulations (Melmed et al., 1988) suggest that the imaged atoms are either the Y or a combination of Cu and O and that the layers observed are those perpendicular to the c-axis (long axis) of the orthorhombic unit cell). It was found that the surface atoms could be field evaporated in a uniform layer-by-layer fashion in either a dc or a pulsed mode. Pulsed field evaporation could be used for atom-probe analysis. An example of an imaging atom-probe mass spectrum from a sample of $YBa_2Cu_3O_{7-x}$ is shown in Fig. 7. The ratio of the species detected is fairly consistent with the known stoichiometry of the material. Detailed studies to determine the microscopic composition fluctuations are now in progress.

Acknowledgements

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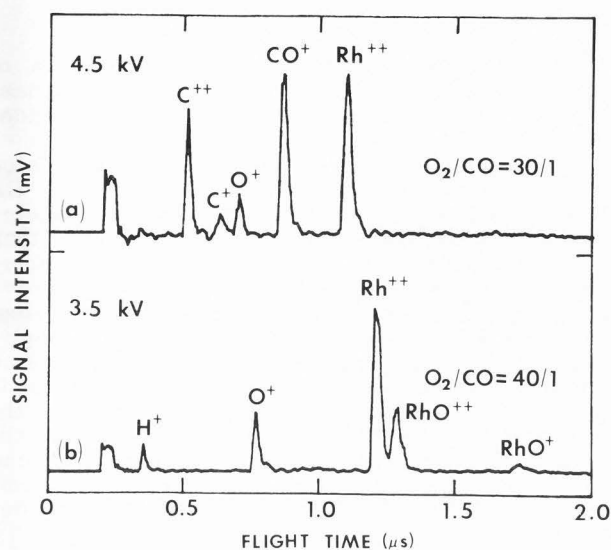


Fig. 5. Representative imaging atom-probe mass spectra from Rh surfaces previously heated to 500 K in mixtures of O_2 and CO. The O_2/CO ratio was 30/1 in (a) and 40/1 in (b). Oxides were detected at O_2/CO ratios of 40/1 and greater which correlates with the ratio for deactivation of the reaction. (Kellogg, 1985c)

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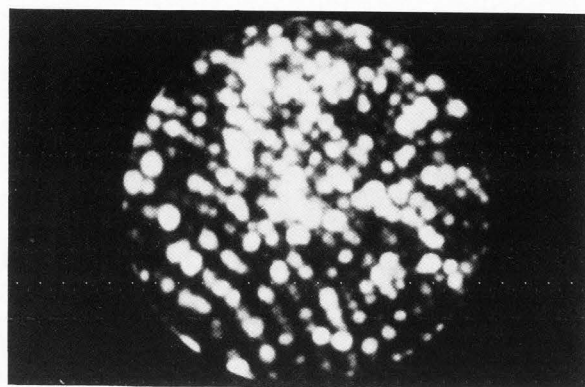


Fig. 6. A field ion microscope image from a sample of superconducting $YBa_2Cu_3O_{7-x}$. The image was recorded in 2×10^{-6} Torr H_2 at 3.9 kV and 50 K. Individual atomic layers can be observed. (Kellogg and Brenner, 1987).

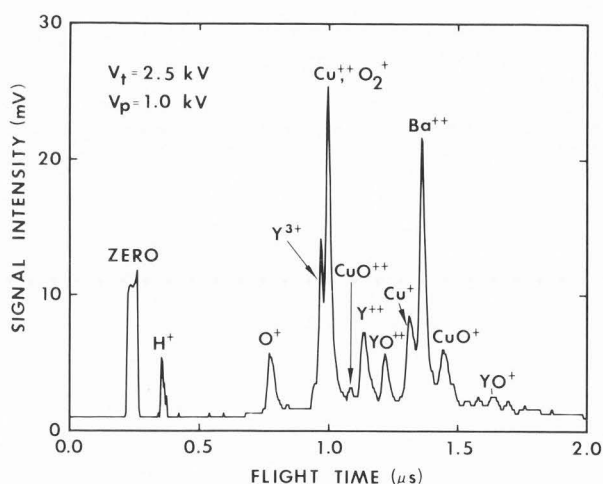


Fig. 7. An imaging atom-probe mass spectrum from a sample of superconducting $YBa_2Cu_3O_{7-x}$. The relative abundances of the detected species are qualitatively consistent with the known stoichiometry of the material. (Kellogg and Brenner, 1987).

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Discussion with Reviewers

B. Ralph: You mention the mass resolution of APFIM and the imaging atom-probe. How important do you think is the incorporation of a Poshenreider analyzer?

Author: By eliminating the energy deficits associated with high-voltage pulse field evaporation, the Poshenreider analyzer can improve the mass resolution of a probe-hole-type atom-probe by better than an order of magnitude. This increased mass resolution is important when examining alloy samples having overlapping isotopes of various charge states, particularly if hydride ions are present. For applications involving materials with well-separated masses, however, the conventional atom-probe is found to be adequate. As an alternative to the Poshenreider analyzer, it has been shown that the use of laser pulses to stimulate field evaporation can improve the mass resolution of a conventional atom-probe even beyond that achieved with a Poshenreider analyzer.

B. Ralph: Are you certain of your identification of the nitride in Fig. 4 as a MoN rather than any other molybdenum based or mixed nitride?

Author: The major species detected in the mass spectrum were singly-charged N, doubly-charged Fe, and doubly- and triply-charged Mo and MoN. In Fig. 4 (b) the gate pulse was set to image the doubly-charged Mo and MoN ions (i.e., a fairly wide gate pulse was used). In Fig. 4 (c) the gate was set to image the doubly-charged Fe ions. Thus, the gated images show directly that the bright regions observed in the field ion image contain Mo and N with little or no Fe. However, the gated images cannot give quantitative information on the composition of the bright regions. In past studies with a probe-hole type atom-probe Brenner and Goodman (1971) identified the bright regions as Fe₃Mo₃N₂ precipitates. The time-gated images indicate that the concentration of iron in the precipitates may be significantly less than this, possibly due to the collection of Fe from the matrix in the probe-hole experiments.