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THE ATOM-PROBE FIELD ION MICROSCOPE: APPLICATIONS IN SURFACE SCIENCE

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The ability to locate an individual atom on a surface, remove it in a controlled fashion, and determine its chemical identity makes the atom-probe field-ion microscope an extremely powerful tool for the analysis of solid surfaces. By itself, the field ion microscope has contributed significantly to our understanding of surface atomic structure, single-atom surface diffusion, and the detailed interactions that occur between atoms and defects on surfaces.¹ When used in combination with the atom-probe mass spectrometer there have been several additional areas within the traditional definition of "surface science" where the chemical identification capability of the atom probe has led to new insights. In this paper these applications are reviewed focusing on two specific areas: surface segregation in intermetallic alloys and chemical reactions on metal surfaces.

The equilibrium distribution of component species in the near surface region of solid solution alloy may be different from the distribution in the bulk. To achieve this distribution, the components in the near surface region redistribute themselves by a phenomenon known as surface segregation. Surface segregation is of both fundamental and technological importance, particularly in the development of bimetallic catalysts. Atom-probe field ion microscope investigations of surface segregation are motivated by the ability to characterize the surface in atomic detail and the exceptionally high depth resolution offered by field-desorption mass analysis. A composition depth profile derived from atom-probe measurements has true atomic-layer depth resolution. These unique capabilities have led researchers to use the atom-probe to study surface segregation in a variety of binary metal alloy systems. In the earliest of these investigations, Ng *et al.*² and Tsong *et al.*³ use the atom-probe to examine surface segregation in the alloy systems Ni-5% Cu and Pt-5% Au, respectively. The results show that in both cases the segregant is the minority species, but the details of the composition profiles depend on the particular alloy system investigated. For the Ni-Cu system the Cu enrichment is confined to the top layer with the second to fifth layers depleted in Cu. In the Pt-Au system, however, the enrichment of Au extends several layers into the near-surface region and the distribution is *oscillatory*. Subsequent atom-probe investigations by Sakurai *et al.*⁴ of the Ni-Cu system extending over a much larger range in alloy compositions, identify an unexpected reversal of the segregant from Cu to Ni when the Ni concentration is less than 0.16. Another interesting effect is the co-segregation of impurity species. Ren and Tsong⁵ show that in Pt-Rh alloys containing sulfur impurities at the 50 ppm level, sulfur atoms segregate to the surface during annealing and induce the co-segregation of Rh. When no sulfur is present the segregant is Pt. The atomic-layer depth resolution of the atom probe is particularly useful in these studies enabling the identification of oscillations in the composition profiles down to a depth of ten atomic layers.

Chemical reactions at solid surfaces are important in a wide range of technologically important processes including corrosion, catalysis, adhesion and lubrication. This importance has stimulated a considerable effort within the surface science community to characterize the detailed, atomic-level processes that underlie surface chemical interactions. Given its ability to locate and identify individual atomic and molecular species on surfaces, the atom-probe would seem to be ideally suited to the investigation of surface chemical reactions. Identification of preferred reaction sites on the surface (e.g., steps and other lattice defects) and determination of reaction intermediates are two obvious applications of the technique. The major problem associated with atom-probe studies of surface chemical reactions is the unknown influence of the applied electric field. For example, pulsed-laser atom probe investigations of the desorption of hydrogen from metal surfaces, in which the field is varied systematically over a range of a few volts/Å, show a continuous change of the detected species from molecular hydrogen to atomic hydrogen.⁶ In this case the dissociation of the

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molecular hydrogen is caused by the applied electric field. The challenge is to separate the field-induced chemistry from the surface-induced chemistry.

One approach to dealing with the electric field is simply to acknowledge its presence and use it to stimulate surface chemical reactions that may not occur otherwise. The formation of H₃ ions and metal-noble gas molecular ions are examples of product species that are formed in the presence of a high electric field.⁷ The details as to how these novel species are formed has stimulated considerable discussion and debate within the field emission community, but are not of general interest to the surface science community. The second approach in dealing with the high electric field is to find ways to avoid it. The earliest atom-probe studies of reactions in which an attempt was made to separate field effects from surface effects were carried out in the laboratory of the late Prof. Block.⁸ In these studies, high-voltage pulses are applied to a tip while exposing it to reactant gases. The pulse amplitude is adjusted such that all species (reactants, intermediates, and products) are desorbed during the pulse interval. In this case, a "field-free" surface chemical reaction takes place during the time interval between pulses. By changing the interval between pulses and measuring the desorbed ion intensities, the reaction rates are determined. This approach has been applied to the adsorption of simple molecular species such as CO, NO and various hydrocarbons, as well as several reaction sequences including the polymerization of diatomic sulfur and formation of Ni carbonyl. The pulsed-laser atom-probe has also been applied to the study of molecular decomposition on surfaces and surface chemical reactions. Here, the ability to vary the electric field over a wider range of field strengths allows one to account for electric field effects. Kellogg's⁹ investigations of CO dissociation on Mo provide a quantitative measure of the activation energy of dissociation and show how the activation energy differs on the flat vs. stepped regions of the surface. Pulsed-laser atom-probe investigations of the N₂-H₂ reaction to form NH₃ by Ai and Tsong,¹⁰ show that the dissociative, rather than the associative mechanism, is responsible for ammonia formation on Pt surfaces. To study surface chemical reactions under conditions similar to those in commercial catalytic reactions, Kellogg¹¹ uses a "high-pressure" sample transfer system which allows one to expose a field emitter tip to reactant gases up to a pressure of one atmosphere and transfer the tip to an atom-probe for analysis. The system has been applied to study the deactivation of the CO oxidation reaction on Rh at high partial pressures of oxygen¹¹ and to investigate the details of surface oxide formation and reduction.¹² The experiments show a nice correlation between the conditions for the deactivation of the reaction and the formation of a stoichiometric oxide on the surface, thus identifying the deactivation mechanism.

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