FIELD ION MICROSCOPY

A Final Report to the

OFFICE OF NAVAL RESEARCH

Contract Nonr-656 (23)

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Department of Physics
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Introduction

The Field Emission Laboratory has been supported by the Office of Naval Research since 1959. Over the past ten years the annual contribution of this contract, Nonr-656 (23), amounted to between 30% and 15% of the laboratory's total operation. The present report summarizes the work done under the ONR contract, lists the publications that have resulted from the work and reports the names of the academic personnel involved in the project.

Summary of Scientific Accomplishments

The objectives of this research have been the development of improved field ion microscopes (FIM), a more complete understanding of the physical principles involved, and the application of the instrument to some specific problems in the physics of surfaces and the properties of metals. The FIM had been conceived by the principal investigator in 1951 and developed to full atomic resolution in 1956. By the time of the beginning of the present ONR contract in 1959, the potential applications had been demonstrated with the imaging of more than a dozen of different metals. At that time, The Penn State Field Emission Laboratory was essentially the only place where field ion microscopy was practiced. (A small group
under M. Drechsler, left behind by the principal investigator in his former laboratory at the Max-Planck Institute in Berlin, contributed some work on tungsten). During the present decade, the FIM became gradually an accepted tool in physical metallurgy and surface physics. All of the important techniques, with the exception of Moore's computer simulation (A. J. W. Moore, J. Phys. Chem. Solids 23, 907 (1962)), have been pioneered in the Penn State Field Emission Laboratory. The results that have emerged from the present contract are described in twenty-five publications. They are listed in the bibliography given below, and the reference numbers in the text of this report refer to relevant papers. Of these publications, seventeen have also been distributed as Technical Reports. At the annual Field Emission Symposia held at various places in the U.S. and twice in Europe, a total of twenty ONR supported papers were presented by our group. Abstracts of these are recorded in the programs of the meetings. The titles of these papers are also listed below as references 26 to 45.

In the initial efforts of this research, we tried to overcome a basic disadvantage of the FIM, its extremely low image intensity. Successful approaches were the dynamic gas supply\(^2\) and the use of an external photo-electronic image intensifier\(^4,5,29\). With both techniques it became possible to obtain a cinematographic recording\(^31\) of the field evaporation process and the emergence of lattice defects at the surface.
Another method of increasing the image brightness was introduced using partial shielding of the tip\textsuperscript{10} to increase the acceleration voltage of the imaging ions.

In the area of image intensification, a considerable progress has recently been achieved in Cambridge, England by ion-electron image conversion using secondary emission from fine wire meshes or in channel plates. Unfortunately, we were unable to participate in this development due to budgetary limitations: Our total equipment budget for the years since 1963 amounted to $640. For this reason we also had to terminate prematurely our original development of a versatile metal FIM\textsuperscript{3,27}. Fortunately, we were able to design a much more advanced instrument with NSF funds, which was used for the ONR contract work for in-situ manipulation of specimens\textsuperscript{15} and several other investigations.

Because of our inability due to budget limitations in pursuing the image intensification problem, we looked for other means of improving the usefulness of the FIM. Immersion of the entire FIM in a liquid hydrogen cryostat\textsuperscript{17} and the measurement of current-voltage characteristics by photometry\textsuperscript{14}, were part of the effort to advance the understanding of the image formation process. The observation of x-rays and of charge exchange\textsuperscript{38} in the FIM also contributed in this direction.

A surprising observation was made with the measurement of the energy distribution in field ionization\textsuperscript{6,32} by a retarding potential technique when it turned out that the half-width of 0.8 eV indicated the origin of the imaging helium
ions to lie within a disc of not more than 0.2 Å thickness floating about 4 Å above the imaged surface atom. To this unexpectedly sharp localization of the ion's origin, we soon added another observation which at first seemed to be impossible to understand with the accepted mechanism of tunneling of an electron from the ground state of the helium atom into the top of the conduction band of the metal. While the field ordinarily required to ionize helium is 450 MV/cm, the adsorption at the metal surface of hydrogen reduced that field to 300 MV/cm. The explanation of this novel effect of hydrogen promotion of field ionization was finally found in the rearrangement of surface charge (E. W. Müller, Surface Sci. 8, 462 (1967)) which occurs when atomic hydrogen is adsorbed in the interstices of sufficiently loosely packed net planes of the metal surface and attracts an electron from an adjacent metal atom to form a hydride-like bond. As a result the metal atom assumes an increased positive charge density and thereby enhances the externally applied field sufficiently to field-ionize the helium image gas atom. The practical advantage of this process is the possibility of imaging a non-refractory metal that ordinarily would field-evaporate at 450 MV/cm at a greatly reduced field strength, while still maintaining the excellent resolution of a helium ion image. The addition of hydrogen also promotes field evaporation of metals, and a delicate balance must be found to utilize the promotion of field ionization without increasing the evaporation rate too much. Complex field induced corrosion effects may
develop in some cases. Hydrogen promotion is now the generally accepted technique for imaging non-refractory metals such as iron, nickel, cobalt, copper and gold.

The proper interpretation of hydrogen promotion of field ionization was only possible after our discovery of the invisibility of cobalt atoms in an ordered Pt-Co alloy. This investigation was originally undertaken because due to the known arrangement of two constituents of the ordered alloys it offered an opportunity of comparing the imaging properties of different atoms. It was now realized that the electronic properties of the surface metal atom is more important than its geometrical position in the surface. The electric field above an adsorbate atom may also be much different from that above the substrate atoms. Thus the limits of the naive image interpretation of geometrical local field enhancement, as expressed in a refined form in the Moore computer model, have now been greatly expanded by including the possible charge rearrangement due to alloy constituents or chemisorbed species. The effects of surface states and of the polarization of the surface atoms upon field ionization and field evaporation are now more clearly seen.

Although our main interest was centered around the development of the FIM and the increased understanding of the physical effects involved, we have also made some efforts towards applications in physical metallurgy. Direct observation of lattice defects is the most important capability
of the FIM. Utilizing its unique atomic resolution, we were the first to investigate a grain boundary in atomic details\textsuperscript{26}. Studies of the initial oxidation of tantalum\textsuperscript{11} revealed the diffusion behavior of oxygen interstitials. We observed some unknown interstitial impurities in rhodium\textsuperscript{36}, while laser-pulse heating of specimen tips\textsuperscript{15,37} produced vacancy clusters, voids, and in iridium a disk like oxygen precipitate.

Considerable efforts were made to investigate the structures of fully and partially ordered Pt-Co and Pt\textsubscript{3}-Co alloys\textsuperscript{16,18,19,22,24,40,42}. Image structures of domains, such as 90-deg orientation domains, antiphase domains and order-disorder domains, are readily identifiable. We found that most of the former interpretation of domain image structures by the Cambridge group was wrong. We were also able to investigate the ordering mechanism of the alloys by annealing of the specimens. Sharp boundaries between the ordered and the disordered phases were directly visible for the first time. We also showed that the ordering parameters, such as the degrees of long range and short range order can be obtained from field ion micrographs. As an example, we calculated the long range order parameter $S$ for a Pt\textsubscript{3}-Co sample to be 0.95 from a counting of the misplaced atoms.

It is quite clear that in field ion microscopy of ordered binary alloys, the techniques for further studies are now well established from our investigation of the platinum-cobalt alloys. What is mostly needed now are advances in the understanding of the field evaporation process. Since the
discovery of this basic physical effect in our laboratory and
the introduction of the image force theory of field evapor-
ation (E. W. Müller, Phys. Rev. 102, 618 (1956)), some progress
has been made\textsuperscript{9,20,25,41,45}, but we do need more experiments as
well as an advanced theory since our latest surprising results
obtained with the novel Atom-Probe FIM (conceived by the prin-
cipal investigator in 1967 and developed in this laboratory
under an NSF grant). We now know that many metals evaporate
as three and four fold charged positive ions (E. W. Müller,
at rates up to $10^9$ layers/sec, and that helium and neon image
gases are field adsorbed at the emitter surface at tempera-
tures as high as 78$^\circ$ K and thereby affect seriously the field
evaporation process (E. W. Müller, Quarterly Rev. \textbf{23}, 177
(1969), E. W. Müller, S. B. McLane and J. A. Panitz, Surface
Sci. November 1969). Clearly, a large unexplored area of
surface physics and high-field effects of gas-surface inter-
actions has been uncovered by the past research, and must be
investigated in the future.
Bibliography of Publications

Resulting from Work under Contract Nonr 656 (23), 1959-1969


Papers Supported from Contract Nonr-656 (23)

Presented at the Annual Field Emission Symposia:


36. Impurity Interstitials in Tantalum and in Rhodium.
E. W. Müller, S. Nakamura, K. Rendulic and S. B. McLane.
12th FE-Symp. Penn State University 1965.

37. Laser Pulse Heating of Emitter Tips. E. W. Müller and
S. B. McLane. 12th FE-Symp. Penn State University 1965.

38. Remarks on the Resolution, the Occurrence of Charge
Exchange and of X-Rays in the FIM. E. W. Müller.


40. FIM Study of the Equiatomic Pt-Co Alloy. T. T. Tsong and


42. FIM Study of Pt-Co. T. T. Tsong and E. W. Müller.

43. Static Field Penetration and Atomic Polarization at a
Metal Surface. T. T. Tsong and E. W. Müller.

44. Localized Surface Disorders by Hydrogen-Neon Image Gas.

45. Further Discussion of Field Evaporation. T. T. Tsong
Personnel

During the period of this report the following academic personnel have been associated with the project:

Principal Investigator:

Dr. Erwin W. Mueller, Evan-Pugh Research Professor of Physics.

Research Associates:

Dr. B. C. Banerjee 1959-1960 (now in India)
Dr. R. D. Young 1959-1960 (now at the Bureau of Standards)
Dr. T. T. Tsong 1966-1969 (Assistant Prof. 1969)

Research Assistant:

S. B. McLane 1961-1969 (MS 1965, Instructor 1967)

Graduate Assistants:

W. Maggee 1963
F. I. Mann 1963
B. J. Waclawski 1959-1961 (MS) (now at the Bureau of Standards)
H. K. Chatterjee 1968-1969 (MS)
The objectives of this project include the development of improved field-ion microscopes, several means of image intensification, and experiments to clarify the physical processes of ion image formation. Applications of field ion microscopy to the study of lattice imperfections and to order-disorder structures of Pt-Co alloys are described. A bibliography containing twenty-five publications and twenty presentations at the annual Field Emission Symposia is given, and the academic personnel connected with this work is listed.