The Atom-Probe Field Ion Microscope*†

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(Received 1 September 1967)

A serious limitation of the field ion microscope has been its inability to identify the chemical nature of the individually imaged atoms. The newly conceived atom-probe FIM is a combination probe-hole FIM and mass spectrometer having single particle sensitivity. During observation, the observer selects an atomic site of interest by placing it over a probe hole in the image screen. Pulsed field evaporation sends the chosen particle through the hole and into the spectrometer section. Preliminary results show that field evaporation of tungsten under poor vacuum conditions occurs as triply or quadruply charged WO, WN, WO_2, and WN_2 ions, while under better conditions doubly and possibly triply charged tungsten can be observed. Mo-Re alloys always produced doubly charged molybdenum and rhenium ions when examined in the atom-probe. Wide applications for the study of short range order in alloys, the chemical nature of precipitates and impurity atoms, and information regarding the imaging properties of various atom species, of both the substrate and adsorbed material, are foreseen.

I. INTRODUCTION

THE field ion microscope[1,2] provides an intimate view of the location of individual atoms on a metal surface. However, its inability to discriminate between different atomic species has been a serious shortcoming. While it is very certain that only one kind of atom is present on pure W, Ir, or Pt surfaces characterized by a highly perfect FIM pattern, it is not possible to unambiguously identify the different atomic species in the usually less regular FIM patterns which are obtained from alloys, crystals containing impurities, or adsorbates at the surface.

It is quite clear that a basic advance in field ion microscopy would be achieved with the identification of the atomic species associated with individual image dots. This difficult task now appears possible with a combination field ion microscope and mass spectrometer having single particle detection capability. Such a device may be called an atom-probe FIM in analogy with the well known electron microprobe developed by Castaing.[3] The latter instrument, a combination electron microscope and x-ray analyzer, can investigate the constituents of a small section of specimen which, although typically of the order of 1 μ in size, still contains some 10^{11} atoms. In the scanning electron microscope developed by Crewe[4] a very crude form of analysis is believed to be possible from the specific energy losses, but the number of atoms involved is still of the order of 10^5.

In the atom-probe FIM we wish to determine the nature of one single atom seen on a metal surface and selected from neighboring atoms at the discretion of the observer.

II. PRINCIPLE

The atom-probe consists of a field ion microscope modified so that the imaged atom chosen for analysis can be positioned over a probe hole in its fluorescent screen. This hole provides an entrance into the analyzer which in the present design is a time-of-flight spectrometer incorporating a detector having single particle sensitivity. After properly positioning the desired atom and pumping the imaging gas from the microscope, a high voltage pulse applied to the tip desorbs the atomic species which then travels through the probe hole. This pulse also initiates the horizontal sweep of an oscilloscope. When the ion reaches the detector a voltage pulse is fed to the oscilloscope, and thus the time-of-flight of the ion is determined. From these data its mass-to-charge ratio can be calculated since the ion acquires essentially its final velocity within a few tip radii, and since the potential difference through which it travels can be accurately measured. The desorption voltage V is, approximately, this potential difference, which is just the sum of the dc imaging voltage and the maximum pulse voltage, since the rise time of the pulse is negligible compared to the time of flight of the ion, and since the pulse amplitude is much less than the imaging voltage.

The mass-to-charge ratio of the detected ion is calculated from the relations

$$\tfrac{1}{2}mv^2=neV \quad \text{and} \quad v=d/t,$$

where m is the mass of the ion, v is its velocity, ne is its charge, d is the distance between tip and detector, and t is the observed time of flight. One finds, for a tip-to-detector distance of 82 cm, that

$$m/n=0.288Vt^2, \tag{1}$$

where m is measured in amu, V is in kilovolts, and t is in microseconds.

* Supported by the National Science Foundation.
† This paper was presented previously at the 14th Field Emission Symposium at the MBS, Washington, D. C. (June 1967).
[1] E. W. Müller, "Field Ionization and Field Ion Microscopy," in *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1960), Vol. 13, pp. 83–179.
[2] E. W. Müller, Science **149**, 591 (1965).
[3] R. Castaing, "Electron Probe Microanalysis," in *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1960), Vol. 13, pp. 317–384.
[4] A. V. Crewe, Science **154**, 729 (1966).

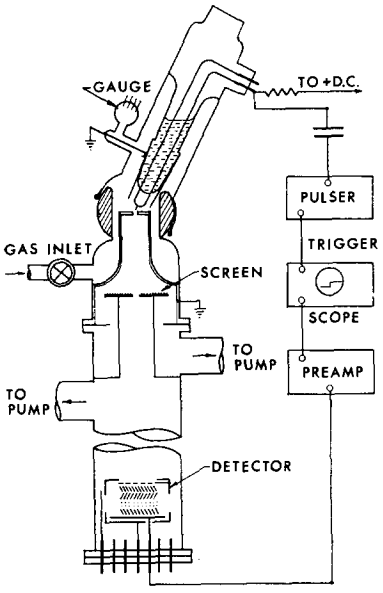

FIG. 1. The atom-probe field ion microscope.

Although our prototype instrument incorporates a time-of-flight analyzer, we are considering the use of other analyzers, including a magnetic sector field with associated multiple detectors. Such a device should permit rapid, consecutive identification of many image spots since the removal of the imaging gas during the desorption process would be unnecessary.

III. A PROTOTYPE ATOM-PROBE FIM

Figure 1 shows a composite view of the atom-probe. During operation the specimen to be examined is mounted on the base of a cold finger and surrounded by an aluminum cone held at ground potential. The cold finger is inserted into the upper portion of the microscope so that the specimen tip is positioned at the center of rotation of the ball joint. When so placed, the tip is axially aligned with respect to the holes located in both the aluminum plate and fluorescent screen. The aluminum plate serves to separate the microscope into two sections. The upper, containing the tip, is connected to a supply of helium gas whose flow rate can be accurately adjusted by means of a variable leak valve. The lower portion containing the fluorescent screen is connected to a liquid nitrogen trapped, 5 cm, oil diffusion pump. During imaging of the specimen, the lower portion of the microscope body is pumped while helium is admitted into the upper portion. This dynamic gas supply system[5] insures that a pressure of about 1 μ is maintained in the immediate vicinity of the tip, while a considerably lower pressure is obtained in the region of the screen.

The time-of-flight tube containing the particle detector and located directly below the fluorescent screen is continuously pumped by a separate, trapped, 5 cm, oil diffusion pump. With the hole size of 1 mm chosen for the fluorescent screen, the vacuum in the vicinity of the multiplier can be maintained, during imaging, at better than 5×10^{-5} Torr. Before actual pulse evaporation the gas supply is shut off and the helium used for imaging is pumped from the microscope ensuring that at a pressure below 10^{-6} Torr an adequate mean free path is obtained.

The evaporation pulse for the atom-probe is taken from a Huggins laboratory pulse generator, model 961-E, having an adjustable pulse amplitude of 0 to 3 kV, a pulse width of 2 nsec, and a rise time and fall time of 0.5 nsec. Manually-triggered single pulses are used in the experiments. The pulse width, rise time, and fall time were confirmed under actual operating conditions by the use of a Tektronix type 519 oscilloscope.

The output of the pulse generator is carried to the microscope head by a 50 Ω coaxial cable terminated by a 50 Ω resistor and coupled to the high voltage leads through a 500 pF, 30 kV capacitor. No attempt was made to clean up reflected secondary pulses as their amplitude is negligible within a period of 100 nsec, which corresponds to less than one mass unit within the voltages likely to be used during normal operation.

The particle detector used is an electron multiplier of the "venetian blind" type, assembled in our Laboratory from 12 dynodes and one anode supplied by EMI (Electrical and Musical Industries, London, England), and baked before use in an auxiliary vacuum system for one hour at 360°C and 10^{-5} Torr. The Be-Cu dynodes are stacked on three ceramic rods and separated from each other by ceramic spacers. They are maintained at appropriate potentials by a resistor chain. A fine wire mesh placed in front of the first dynode and separared from it electrically by two 2 MΩ carbon resistors provides a means of accelerating the incoming ion slightly before striking the first dynode. An electropolished nickel cap covers the mesh and first two dynodes. It is maintained at the same potential (−3000 V dc) as the wire mesh and serves to discourage field emission from possible sharp edges on those initial dynodes held at large negative dc potentials. The entire multiplier is rigidly mounted on an O-ring flange bolted to the base of the time-of-flight tube. All external electrical connections including the multiplier output are made through ceramic-to-metal seals soldered to the flange.

The output of the particle detector is connected to a transistorized preamplifier with an input resistance greater than 10^8 Ω and an output resistance of less than 500 Ω. The detector-preamp combination provides an over-all current gain of greater than 10^{12}. Tests with a Tektronix type 519 oscilloscope showed that for capacitive coupling the preamplifier has a frequency response in excess of 200 MHz. The 16 nsec rise time of the Tektronix type 551 oscilloscope, used to measure the time of flight, determined the rise time of the pulse; the fall time of 1 msec was determined

[5] B. Waclawski and E. W. Müller, J. Appl. Phys. 32, 1472 (1961).

by the detector-preamplifier combination. However, this did not limit the usefulness of the combination in resolving adjacent masses, as a staircase wave shape resulted when two or more particles reached the detector during a single sweep. The resolution of the present equipment is about 1 to 2 atomic mass units, entirely sufficient for our preliminary investigations.

At the maximum current sensitivity of the preamplifier-oscilloscope combination, some 5 pA/cm, no dark current noise was perceptible from the detector. However, on slow sweeps a few random events (of the order of one per second) could be detected, and when small amounts of helium were admitted to weakly image the specimen, helium ion pulses were observed in the expected numbers. Using the normal single sweep of 10 μsec which covers all masses of possible interest, and even with only a modest background vacuum of 10^{-6} Torr, a noise signal that could be mistaken for a desorbed ion was never encountered.

Figure 2(a) shows an example of the oscilloscope pattern obtained from the atom-probe examination of tungsten for two different tip voltages. As can be seen, the rise time of the pulse is quite short, but since the sweep is 1 μsec/cm, the decay time of 1 msec produces a horizontal line. The amplitude of the initial transient could be decreased by more thorough shielding, but was ignored since it did not saturate the preamplifier. The initial oscillations were damped in a time shorter than required for the transit of any possible species appearing on the surface of the specimen and were, therefore, also ignored.

IV. EXPERIMENTAL RESULTS

Using Eq. (1) we find for the upper trace in Fig. 2(a) $m/n=71$, and for the lower trace (from left to right) $m/n=53.6$, and $m/n=71.2$. Because of the relatively poor vacuum conditions maintained at the tip (due to the presence of the greased ball joint and an insufficient path for evacuation), we believe ourselves justified in identifying these species as the tungsten-oxygen complexes $^{182}W^{16}O_2^{+++}$ ($m/n=71.3$) and $^{184}W^{16}O_2^{++++}$ ($m/n=54.0$). Both have been observed previously by other experimenters engaged in more conventional mass spectrometry of oxidized tungsten at elevated temperatures using a field ionization emitter.[6] However, in view of the well known occurrence of nitrogen etch[7] in insufficiently evacuated field ion microscopes, the two species observed may also represent three and four-fold charged ions of $^{186}W^{14}N_2$ molecules, and the ion with $m/n=71.2$, $^{182}W^{14}N_2^{+++}$.

Because of the preliminary design of the present system it was impossible to photograph the screen both before and after evaporation to obtain a precise indication of the location of the species being examined. In the lower trace, clearly, the probe hole was situated so as to allow two neighboring species to be detected. This condition is quite reproducible and, in fact, was observed at other tip voltages, as well as for other tips of the same material imaged in an identical manner.

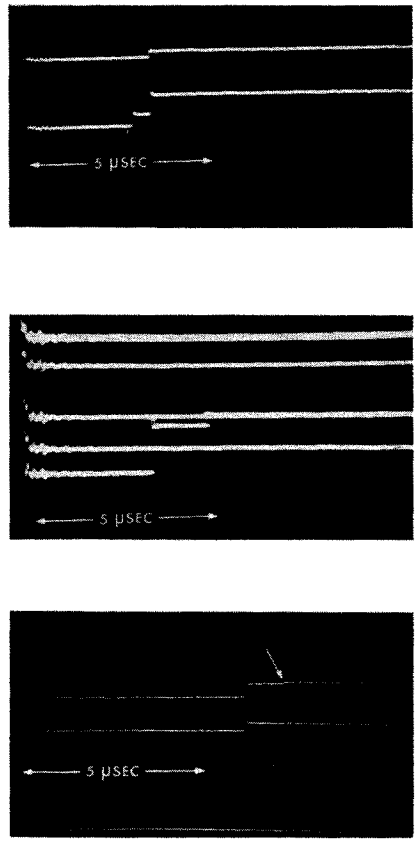

FIG. 2 (a) Atom-probe examination of tungsten; upper trace—25 kV dc +2.4 kV pulse; $m/n=71$ ($t=3.0$ μsec). Lower trace—25 kV dc+2.5 kV pulse;(from left to right) $m/n=53.6$ ($t=2.6$ μsec), $m/n=71.2$ ($t=3.0$ μsec). (b) Atom-probe examination of a rhenium molybdenum alloy; 15.5 kV dc+1 kV pulse; (from left to right) $m/n=48$ ($t=3.2$ μsec), $m/n=93$ ($t=4.4$ μsec). (c) Atom-probe examination of tungsten; Upper trace—9 kV dc+0.2 kV pulse; (from left to right) $m/n=66$ ($t=5.0$ μsec), $m/n=91$ ($t=5.8$ μsec). Lower trace—9 kV dc +0.2 kV pulse; $m/n=66$ ($t=5.0$ μsec).

Figure 2(b) shows the result of using the atom-probe to examine a rhenium-molybdenum alloy, field evaporated at 78°K. Here, once again, is one of a series of photographs in which two atomic species were detected. In this photograph, the smaller ratio (corresponding to the shorter time) is $m/n=48$, while the larger ratio is $m/n=93$. These correspond, respectively, to $^{96}Mo^{++}$ and Re^{++}. The mass-to-charge determination is accurate to about ± 1 amu.

Figure 2(c) resulted from an examination of tungsten at 21°K. A getter had been installed near the tip to improve the vacuum conditions during desorption. Both traces resulted from an imaging voltage of 9 kV, and a pulse voltage of 200 V. Using Eq. (1) one obtains for the upper trace (from left to right) $m/n=66$ and $m/n=91$. For the

[6] R. Vanselow and W. A. Schmidt, 12th Field Emission Symposium (The Pennsylvania State Univ., 1965).

[7] J. F. Mulson and E. W. Müller, J. Chem. Phys. 38, 2615 (1963).

lower trace $m/n=66$. We believe $m/n=91$ corresponds to $^{182}W^{+++}$ while $m/n=66$ corresponds, most probably, to $^{182}W^{16}O^{+++}$ or $^{184}W^{14}N^{+++}$. Of some thirty traces resulting from four specimen tips, W^{++} was observed on only three occasions. The majority of the remaining traces were the tungsten-oxygen or tungsten-nitrogen complexes described earlier. A mass-to-charge ratio between 62.9 and 64.6 was obtained in five cases. This might correspond to $^{186}W^{+++}$ ($m/n=62$), or perhaps to $^{182}W^{14}N^{+++}$ or $^{182}W^{16}O^{+++}$ with $m/n=65.3$ or 66, respectively. Because of the remaining uncertainty of interpretations, no definite conclusions could be drawn, at this time, about the relative abundances of W^{++} and W^{+++}.

V. DISCUSSION

The results obtained to date with the prototype atom-probe, although limited in scope, are highly successful in that they show the feasibility of this most sensitive mass spectrometer, as well as provide a basis on which to design a more sophisticated instrument. Certainly, our experience has shown that it must include such necessary refinements as an adjustable probe hole, and a means to accurately photograph the image both before and after pulse evaporation. In addition, it seems necessary to employ a grease-free, all metal, ultrahigh vacuum system so as to minimize possible tip contamination. These considerations have been incorporated into an instrument which is now being constructed in our Laboratory.

What can be expected of the new technique? It should now be possible to settle the controversy among field ion microscopists concerning the nature of the bright spots obtained by adsorption of oxygen, nitrogen, and carbon monoxide, which have been suggested as representing either adsorbates[8] or tungsten atoms displaced by the corrosion process.[9,10] We will be able to identify the chemical complexes involved in water-etch[7] and oxygen corrosion,[9] as well as the products of reactions initiated under the extreme electric fields encountered at the surface of a specimen. We believe we now have a powerful tool for alloy research since we can determine, quite easily, short range order, discrete visibility of atomic species,[11] and other related items of interest. Finally, the chemical nature of interstitials, segregations, and precipitates will be open to direct experimental observation and analysis.

[8] G. Ehrlich, Discussions Faraday Soc. **41**, 55 (1966).
[9] E. W. Müller, "FIM Studies of Surface Corrosion of Interstitials, Vacancies and α-Irradiation Damage by Controlled Field Evaporation of Atomic Layers," in *Structure and Properties of Thin Films*, C. A. Neugebauer, J. B. Newkirk, D. A. Vermilyea, Eds. (John Wiley & Sons, Inc., New York, 1959), p. 476.
[10] A. A. Holscher and W. M. H. Sachtler, Discussions Faraday Soc. **41**, 29, 54, 70 (1966).
[11] T. T. Tsong and E. W. Müller, Appl. Phys. Letters **9**, 7 (1966).

THE REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 39, NUMBER 1 JANUARY 1968

Recording Fabry-Perot Interferometer

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(Received 26 July 1967; and in final form, 19 September 1967)

A recording interferometer is described in which a direct plot of spectral intensity against wavenumber is obtained without the use of a time base. When used as a double recorder, the instrument records two spectral profiles simultaneously. In this form, the recorder is particularly suited to the comparison of spectral profiles and the measurement of small line shifts.

INTRODUCTION

PHOTOELECTRIC recording is now a well established technique of interference spectroscopy. In the most widely used method,[1,2] the optical path in a Fabry-Perot etalon is varied by changing the pressure of the gas between the plates, and the intensity at the center of the fringe pattern is plotted against time by means of a chart recorder. To obtain a linear wavenumber scale, it is necessary to vary the pressure at a constant rate. The difficulties involved in controlling the pressure variation to the required degree of accuracy led to the development of the direct-recording interferometers now in use at the Clarendon Laboratory. These avoid the necessity for a time base, since the intensity in the center of the fringe pattern is plotted directly against the pressure in the etalon box.

The recorders have now been in use for several years in investigations requiring the detailed analysis of spectral

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[2] P. Jacquinot, Rept. Progr. Phys. **23**, 267 (1960).