resistor whose characteristics are shown in Fig. 11. At $T=4.50$ K and $H=145$ kG we have, from Fig. 9, $\Delta R/R_0=0.131$ and $\partial(\Delta R/R_0)/\partial T=-0.025$ $(K)^{-1}$. The sensitivity at $T=4.50$ K and $H=0$ is $S=-0.323$ $(K)^{-1}$. Substituting these values into Eq. (7) we obtain $S=-0.345$ $(K)^{-1}$ at $T=4.50$ K and $H=145$ kG in agreement with the previous procedure.

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Calibration of the Atom Probe FIM*

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Accurate identification of atomic species in the atom probe FIM requires a highly shielded tip assembly, as well as a revision of the equation formerly used to compute the m/n ratios. Voltage reflections on the unterminated pulse transmission line cause the actual evaporation pulse at the tip to be greater than the applied pulse by a "pulse factor" α. In addition, the recorded flight time of the ion under investigation differs from the actual flight time by a constant electronic time delay δ. Using either of two single isotope calibration techniques, both α and δ can be determined. For a shielded tip assembly either technique gives a value of $\alpha=2.00\pm0.05$ and a value of $\delta=0.06\pm0.02$ μsec. Typical absolute mass determination using these values of α and δ is within ±0.6 amu at $m/n=20$, and ±1.6 amu at $m/n=100$. When masses near a known species, like hydrogen- or helium-metal molecular ions, are to be detected, the practical resolution reaches ±0.2 amu at the middle of the mass range.

INTRODUCTION

THE ultimate tool for microanalytical research would be an instrument capable of identifying single atoms chosen at the discretion of the experimenter as he examines an atomically resolved specimen surface. Within certain limits, the atom probe FIM[1,2] can do just this. The limitations on the instrument's utility are set, primarily, by three considerations: the type of material which can be successfully examined in a field ion microscope, the method used to separate, and the method used to identify the selected species from its surroundings. It is the purpose of this paper to investigate in some detail the latter consideration, and in doing so to present methods for the calibration of the instrument.

PRINCIPLE

The operating principles of the atom probe field ion microscope were discussed in our previous papers.[1,2] The metal specimen under examination is placed in a modified field ion microscope (Fig. 1) and imaged in the usual manner.[3] After adjusting the specimen to properly position the desired surface atom over a probe hole in the microscope's phosphor coated screen and pumping away the imaging gas if desired, the specimen is subjected to a field evaporation pulse. Only the atom which was imaged over the probe hole passes as an ion into the time-of-flight tube, the others being blocked by the screen. After traveling approximately 1 m, the ion arrives at a 12-stage electron multiplier, producing a signal which is displayed on an oscilloscope. The recorded sweep, initiated by the evaporation pulse, is, therefore, a measure of the time-of-flight of the ion. If the duration of the evaporation pulse has been longer than the ions' travel time in the acceleration region near the tip, the evaporated ion will have attained a kinetic energy determined solely by the sum of the dc imaging voltage and the pulse evaporation voltage, that is,

$$\tfrac{1}{2}mv^2=ne(V_{\rm dc}+V_{\rm pulse}), \tag{1}$$

where ne is the ion's charge and v its velocity. Since the field rapidly diminishes with distance from the tip, the ion has acquired this kinetic energy within the first 1 or 2 mm of its path and from there on travels in field-free regions with a constant velocity. The travel time is approximately

$$\tau\cong d/v, \tag{2}$$

where d is the tip-to-detector distance. The selected ion is identified by its mass-to-charge ratio expressed in

* Supported by the National Science Foundation.
[1] E. W. Müller, J. A. Panitz, and S. B. McLane, Rev. Sci. Instrum. 39, 83 (1968).
[2] E. W. Müller, S. B. McLane, and J. A. Panitz, in *Electron Microscopy 1968*, D. S. Bocciarelli, Ed. (Tipografia Poliglotta Vaticana, Rome, 1968), Vol. 1, p. 135.
[3] E. W. Müller, Advan. Electron. Electron Phys. 13, 129 (1960).

terms of the total voltage and travel time. For our instrument, with $d=0.995$ m, one finds from (1) and (2)

$$(m/n)_0=0.195(V_{dc}+V_{pulse})\tau^2, \quad (3)$$

where V_{dc} and V_{pulse} are measured in kilovolts and τ is measured in microseconds.

FURTHER CONSIDERATIONS

Equation (3) was derived using several simplifying assumptions which are not satisfied in practice. If the ion after acquiring the energy $ne(V_{dc}+V_{pulse})$ is additionally accelerated in a region of attractive potential $-V(x)$ in front of the multiplier detector, one can show that Eq. (3) must be rewritten

$$m/n=0.195(V_{dc}+V_{pulse})\tau^2\beta=(m/n)_0\beta, \quad (4)$$

where

$$\beta\equiv\left[\frac{1}{d}\int_0^d \frac{dx}{\{1+[v(x)/(V_{dc}+V_{pulse})]\}^{\frac{1}{2}}}\right]^{-2}, \quad (5)$$

and x, in meters, is measured from the detector. In our original instrument, the accelerating field of the detector extended approximately 10 cm into the time-of-flight tube. The actual potential distribution was measured using a full scale model in an electrolytic trough in order to evaluate the integral in Eq. (5). For the extreme case of a slow ion with $V_t=4.0$ kV and a multiplier potential of 4.0 kV, Eq. (4) predicts a 2.2% increase in the value of m/n computed from Eq. (3). If a grounded wire mesh is placed 1 cm from the multiplier, the increase in m/n is reduced below 0.4% and is completely negligible for larger ion energies.

The important point is that any stray fields will affect the ion's energy and therefore the apparent mass-to-charge ratio that is determined. In addition, lateral components near the tip during pulsing may seriously affect the ion's trajectory causing an ion other than the one originally imaged on the probe hole to be recorded. For this reason special care must be taken to provide adequate shielding of the specimen. Figure 1 shows a schematic diagram of the improved atom probe.[2] A metal bellows and a rotatable stainless steel and glass standard taper joint permit extreme movement of the specimen. A grounded copper cylinder which is rigidly fastened to the bellows surrounds the cold finger, while the tip and its mounting coils are enclosed in a separate copper cylinder.

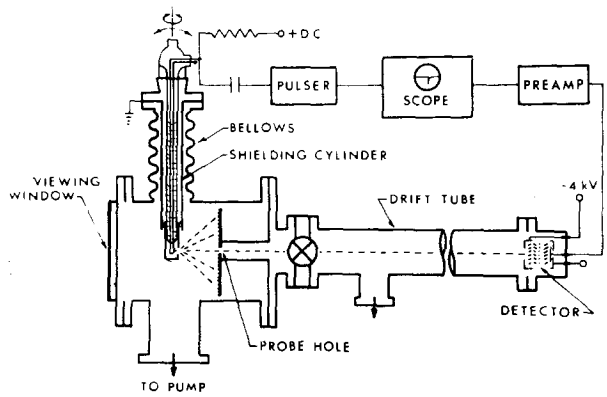

FIG. 1. The atom probe field ion microscope.

This cylinder is in thermal contact with the cryogenic fluid in the cold finger and is electrically grounded to the other copper cylinder by beryllium-copper leaf springs. A small aperture permits the ions to reach the screen. The entire cold finger assembly can be rotated within the copper tube while preserving electrical contact with it. Since the dc imaging voltage and positive evaporation pulse travel to the specimen inside these grounded enclosures, field penetration into the main body of the microscope is reduced to a negligible amount. We have experimented with several other designs incorporating open, unshielded tip assemblies. In each case the field surrounding the electrode structure seriously influenced the ion's trajectory. Successful aiming at the probe hole is especially difficult (if not impossible) when one induces evaporation by negatively pulsing a small unshielded annulus concentric with the tip, an electrode arrangement first used by Brenner and McKinney.[4] By using an FIM with such an electrode arrangement and applying a negative dc voltage to the ring and screen electrode as a long time "pulse," sections of the image shift by as much as 10 atomic diameters. This is caused by the typical variation of the image compression factor in a three electrode system, the third electrode being the grounded wall of the FIM that "sees" the beam. It is important to reemphasize that a well defined ion trajectory so critical to successful identification of a preselected atom in the atom probe can only be achieved by limiting, to a negligible amount, lateral field components, particularly those that may change during the pulsing time. For this reason a highly shielded tip assembly such as the one shown in Fig. 1 is essential.

The selected atom is evaporated, typically, by means of a 20 nsec positive high voltage pulse. This pulse is coupled to the specimen through a capacitor connected to the dc line outside the cold finger. After passing through this capacitor the pulse must travel to the specimen which forms, for practical purposes, the unterminated end of a cylindrically symmetric transmission line. The center electrode of this line is the leads ending with the specimen, while the outer electrode is the grounded copper shielding tube and grounded copper housing. Such an unterminated line is characterized by voltage reflections. Unfortunately, the line cannot be terminated to eliminate these reflections because of the high dc imaging voltage present at all

[4] S. S. Brenner and J. T. McKinney, Appl. Phys. Lett. 13, 29 (1968).

times. As a result, if the initial pulse is of sufficient duration these reflections will add to it producing, at the specimen, an effective pulse whose amplitude is greater by some factor α than the initial pulse. This "pulse factor," which has been observed experimentally, will be constant for a constant line geometry and will require Eq. (3) to be modified as follows:

$$(m/n)_0=0.195(V_{dc}+\alpha V_{pulse})\tau^2. \quad (6)$$

Moreover, due to electronic delays, the travel time τ is not directly recorded on the oscilloscope. What is recorded is the observed time t, where

$$t=\tau\pm\delta, \quad (7)$$

and δ is the total electronic delay time.

Equation (3) can now be written in its final form,

$$(m/n)_0=0.195(V_{dc}+\alpha V_{pulse})(t\pm\delta)^2. \quad (8)$$

It is assumed, of course, that V_{dc} and V_{pulse} are accurately known. Fortunately, at least two independent methods exist to determine the correction factors α and δ, thereby calibrating the atom probe. Both methods rely upon a previous knowledge of the evaporated species, but such knowledge is possible since several single isotope metals exist which are suitable for imaging in the field ion microscope. One of these, rhodium ($m=103$), has been used extensively in our present work.

CALIBRATION

Suppose that a rhodium tip is used for the calibration experiment, and that pulse evaporation is conducted in high vacuum after having first established a perfect rhodium pattern in the presence of an imaging gas. If a single sufficiently large pulse is used, many atom layers will field evaporate. Provided the total voltage is kept constant, continued pulsing will consistently produce two mass spikes at the same points in time. These could only represent rhodium ions of different charge. Applying Eq. (8) to each observed mass, and dividing, we find

$$\frac{(m/n)_2}{(m/n)_1}=\frac{t_2^2\,(1\pm\delta/t_2)^2}{t_1^2\,(1\pm\delta/t_1)^2}\cong\frac{t_2^2\,(1\pm2\delta/t_2)}{t_1^2\,(1\pm2\delta/t_1)}. \quad (9)$$

Setting $\delta=0$ as a first approximation and substituting the recorded values of t_1 and t_2, one finds

$$(m/n)_2/(m/n)_1\cong1.5. \quad (10)$$

This is just the ratio expected for doubly and triply charged ions of the single isotope metal. Figure 2 shows a typical photograph obtained during such an experiment. Note that a 10 MHz time calibration trace appears on the photograph. This trace, obtained from an oven controlled crystal oscillator, provides a time calibration independent of the oscilloscope's time base generator.

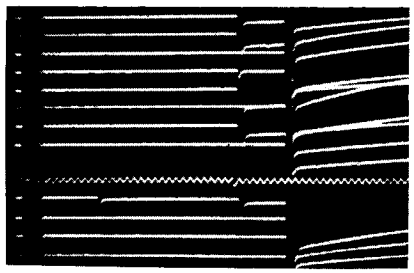

FIG. 2. Rh^{3+} and Rh^{2+} at 21 K and 5×10^{-8} Torr. $V_{dc}=14.8$ kV, $V_{pulse}=2.0$ kV. The early spike below the time trace represents mass 4, adsorbed He.

Now, applying Eq. (8) to each of the two rhodium ions which appeared on a single sweep and solving the simultaneous equations for the pulse factor, one obtains

$$\alpha=\frac{\{[(m/n)_2]^{\frac{1}{2}}-[(m/n)_1]^{\frac{1}{2}}\}^2}{0.195V_{pulse}\Delta t^2}-\frac{V_{dc}}{V_{pulse}}, \quad (11)$$

where $\Delta t=t_2-t_1$ is the time difference between the two mass spikes, and V_{dc} and V_{pulse} are accurately known. Combining Eqs. (8) and (11) and solving for the time delay gives

$$\delta=t_2-\Delta t\{1-[(m/n)_1/(m/n)_2]^{\frac{1}{2}}\}^{-1}. \quad (12)$$

This method, then, allows α and δ to be calculated and the atom probe to be calibrated if at least two known masses appear on a single trace. If a third mass is also known the method can be applied to each of the three measurable time differences, and an average of δ and α computed. Finally, if unknown masses appear on the same trace, they can be determined with a great degree of accuracy since both the total voltage and the "time correction" δ are known.

In practice, α and δ for our instrument have been determined by the above method using both the Rh^{2+} and Rh^{3+} spikes, as well as other "calibration" peaks. For example, by admitting hydrogen to the microscope and momentarily reducing the dc to encourage absorption on the specimen, both H^+ and Rh^{2+} can be observed on a single trace. The danger here is that what one takes as an Rh^{2+} ion may actually be an RhH^{2+} or an RhH_2^{2+} molecular ion.[5] The advantage of not using Rh^{3+} as one of the calibration masses is that Rh^{2+} is significantly more abundant and can be obtained readily by a gentle evaporation of the specimen. If Rh^{3+} is desired on the same trace, many layers must be evaporated within one pulse to insure, statistically, that some Rh^{3+} will be formed and pass through the probe hole. The required evaporation rates are quite high, up to 10 surface layers per nanosecond or $2\frac{1}{2}$ m of metal per second.

A second independent method can be used to calculate a value for α and δ. It also assumes a previous knowledge of the evaporated species, but unlike the previous method it requires only one known mass for calibration. As a

[5] D. F. Barofsky and E. W. Müller, Surface Sci. **10**, 177 (1968).

result, if a single isotope metal is investigated, the pulse evaporation can be very gentle.

Let us assume that rhodium is evaporated in high vacuum after establishing a perfect pattern in an imaging gas. The pulse voltage is set and the dc voltage raised until ions are detected during each pulse. Pulsing is continued and the dc voltage raised slightly until consistent masses are observed indicating that the abundant ion, Rh^{2+}, is being detected. This procedure is continued for several pulse voltages; the pulse voltage is changed only after 20 or 30 consistent masses have been recorded.

Each consistent mass is known to be Rh^{2+}, corresponding to an m/n of 51.5. This is the value of m/n which Eq. (8) must predict. We are interested, therefore, in minimizing the difference between 51.5 and the value predicted by Eq. (8) for each consistent mass. In minimizing this difference, the square of the difference is also minimized. That is, for n recorded masses, the quantity

$$\sum_n [51.5-0.195(V_{dc}+\alpha V_{pulse})(t+\delta)^2]^2 \qquad (13)$$

is to be minimized with respect to the unknowns α and δ. Therefore

$$(\partial/\partial\alpha)\sum_n [51.5-0.195(V_{dc}+\alpha V_{pulse})(t+\delta)^2]^2=0 \qquad (14)$$

$$(\partial/\partial\delta)\sum_n [51.5-0.195(V_{dc}+\alpha V_{pulse})(t+\delta)^2]^2=0, \qquad (15)$$

where V_{dc} and V_{pulse} may vary for each mass, but are known. The simultaneous Eqs. (14) and (15) may be solved numerically for α and δ by using the Newton–Raphson method. The mathematical procedure is straight forward[6] and one finds that the values obtained for α and δ do not depend upon the initial values used to initiate the solution, provided, of course, that physically reasonable numbers are used. This means that initially α can be set to equal 1, and δ set equal to zero, and the method will rapidly converge to the true values.

NUMERICAL RESULTS

The pulse factor α and the time delay δ have been determined, using the single isotope metal rhodium and both calibration methods. For our instrument a consistent value of $\alpha=2.00\pm0.05$ is obtained. This value does not depend upon the masses chosen for calibration or the type of coolant employed; however, it does depend on the exact geometry of the tip end of the pulse transmission line. For example, by opening the small aperture in front of the tip to the full diameter of the shielding cylinder, the pulse factor changes to 1.40. The value obtained for δ is typically 0.06 ± 0.02 μsec. The apparent variation in the time delay is due in large measure to the time sweep of the oscilloscope currently used in this work. Successive sweeps displaying a 10 MHz (±60 Hz) calibration signal show time differences of ±0.02 μsec. Since this is within the specified accuracy of the oscilloscope, another more accurate and reproducible method of timing the ions' flight is needed. A solid state timer incorporating multiple registers is being built to meet these requirements.

The fractional error in m/n predicted from Eq. (8) is

$$\frac{\Delta(m/n)_0}{(m/n)_0}=\frac{V_{pulse}}{(V_{dc}+\alpha V_{pulse})}\Delta\alpha+\frac{2}{(t+\delta)}(\Delta t+\Delta\delta), \qquad (16)$$

assuming that the error in the measured values of V_{dc} and V_{pulse} is negligible. $\Delta\alpha$ and $\Delta\delta$ are typically ±0.05 and ±0.02, respectively, while because of the oscilloscope sweep $\Delta t=\pm0.02$. Therefore, for ions with (V_{dc} and αV_{pulse}) $=10$ kV and $V_{pulse}=1$ kV, the error in the mass determination is, approximately, ±0.6 amu for $(m/n)_0=20$ amu, and ±1.6 amu for $(m/n)_0=100$ amu.

Fortunately the resolution can be greatly improved if multiple masses appear on a single trace provided one mass spike can be identified. In such instances Eq. (11) can be used to predict the other masses in terms of the known species and the measured time differences which are independent of the time delay δ and its associated error.

A further increase in resolution is obtained by using an oscilloscope which permits any selected portion of its sweep to be expanded in time. With this feature and a 2 m time-of-flight tube the typical resolution is ±0.2 amu at $(m/n)_0=50$ amu. This is quite sufficient to unambiguously distinguish metal ions from metal–helium molecules[7,8] and the frequently occurring metal hydrides.[5] These molecular compounds (the former having been first observed with our instrument) require the highest resolution that can be reasonably expected from a time-of-flight mass spectrometer operating with ions in the 10 keV energy range.

ACKNOWLEDGMENTS

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[6] J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, 1966), p. 215.

[7] E. W. Müller, Quart. Rev. (London) **23**, No. 2, 177 (1969).

[8] E. W. Müller, S. B. McLane, and J. A. Panitz, Surface Sci. (to be published).