

FIELD-ION ENERGY ANALYSIS
AND FIELD-DESORPTION MICROSCOPY

by

Allen Robert Waugh
Pembroke College
Cambridge

A dissertation
submitted for the degree of Doctor of Philosophy
in the University of Cambridge

March 1975

Preface.

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Preface.

This dissertation is submitted for the degree of Doctor of Philosophy in the University of Cambridge. The research described was carried out during the period from October 1971 until December 1974, in the Department of Metallurgy and Materials Science, University of Cambridge, under the supervision of Dr. M.J. Southon.

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My thanks are due to the Science Research Council for providing a maintenance grant and for financing the research, to the Paul Instrument Fund of the Royal Society for the provision of apparatus, and to Professor R.W.K. Honeycombe for the provision of laboratory facilities.

The experimental and theoretical work described in this dissertation is, to the best of my knowledge, original except where reference has been made to the work of others. This dissertation is not substantially the same as any that I have submitted for a degree or diploma or other qualification at any other University. Further, no part of this dissertation has already been, or is being concurrently, submitted for any such degree, diploma, or other qualification.

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Chapter 1.INTRODUCTION.LIBRARY
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This dissertation is concerned with the development and application of new experimental techniques in Field-Ion Microscopy, with the intention of clarifying some of the physical processes involved in field-ion image formation and in field-evaporation; that is, in the interaction of a curved metal surface with a very high electric field, in the presence or absence of an inert gas. The techniques employed include simple field-ion imaging, field-desorption imaging, ion current measurements, energy analysis and atom-probe mass-spectrometry. Results are derived which are not predicted by present field-evaporation theories and which must be considered in future theories: operating boundary conditions for the atom-probe are also described.

1.2 Field-Ion Microscopy.

Field-ion microscopy was invented by Professor E.W. Muller in 1951. In this technique the specimen to be studied is the hemispherical end-cap at the tip of a sharply-pointed metal or semi-metal needle; the end-cap is typically 10-200 nm. in diameter. In the field-ion microscope (FIM) the specimen needle is positioned some tens of millimetres from a phosphor screen: a high positive potential (1-30 KV) is applied to the specimen, creating a very high electric field ($1-5 \cdot 10^{10} \text{ V m}^{-1}$) at its tip. This field ionizes any gas present near the tip and repels the positive ions formed towards the screen, where they produce scintillations. As ions are formed preferentially over atoms protruding from the surface and the ions are repelled radially

to the screen, the scintillations map out the surface atomic arrangement on the tip of the needle. Cooling the tip to 78°K or below increases the resolution of the instrument, by reducing tangential velocities of the gas ions, so that close-packed atoms in the surface may be resolved. In modern field-ion microscopes a micro-channel-plate image intensifier (Turner et al 1970) is generally interposed between the specimen and the phosphor screen; this device converts the flux of gas ions into an amplified flux of electrons, which are more efficient at exciting the phosphor and which do not damage it.

The electric field may be raised to a level high enough to ionize protruding surface metal atoms and remove them from the surface: this is termed 'field evaporation'. Field evaporation is used to create the initial smooth endcap of the specimen from a roughly electropolished wire and to dissect the specimen, uncovering features of interest lying in the bulk of the metal below the initial surface. By pulsing the field to a high value for a short time, individual ions removed from the surface may be chemically analysed in a time-of-flight mass spectrometer; this is the 'Atom-Probe' field-ion microscope, also invented in Muller's laboratory (Muller et al 1968). For a comprehensive review of the early development of field-ion microscopy and some of its applications to surface physics and metallurgy the reader is referred to the book by Muller and Tsong on the subject, and to their later review (Muller and Tsong 1969, 1973). Only previous work which is directly relevant to this dissertation will be reviewed in this chapter and elsewhere, as the literature is large.

1.3 Field Evaporation.

Although field evaporation is used in all experiments involving field-ion microscopy, the physical processes involved are not well understood at the present time. The interaction of an electric field of $2-6 \times 10^{10}$ volts/metre with the atoms on a metal surface is a difficult process to treat theoretically. Nonetheless, various attempts have been made to tackle the problem (Muller 1956, Gomer 1959, Gomer and Swanson 1963a,b, Brandon 1965) and various attempts to refine these theories will be described below.

1.3.1 The Image-Force Theory.

The simplest theory of field-evaporation treats it as the removal of a surface atom, as an ion, over the Schottky barrier formed by the combined effect of the potentials due to the external field and to the coulomb attraction between the ion and its image in the metal. This gives a barrier Q_n to evaporation, where

$$Q_n = \Lambda + \sum_n I_n - n\phi - \frac{(n^3 e^3 F)^{1/2}}{(4\pi\epsilon_0)} \quad (1)$$

for an ion of charge n ; here Λ is the sublimation energy of a surface atom, I_n is n^{th} ionization energy of a free atom, ϕ is the work function of the metal, and F is the field.

The ion is thermally excited over this barrier; the rate constant for this process is

$$k_e = \nu \exp(-Q_n/kT) \quad (2)$$

where ν is the atomic vibration frequency and k is Boltzmann's constant. (1) and (2) may be combined to give

$$F = \frac{4\pi\epsilon_0}{3e^3} \left(\Lambda + \sum_n I_n - n\phi + kT \ln \frac{k_e}{\nu} \right)^2$$

The charge species to be expected may be found by minimizing

F with respect to n , at constant k_e (Brandon 1965). If this is done using reasonable values for the parameters involved (Taylor 1970) it is found that $n = 2$ for most metals, with the exception of tungsten, for which $n = 3$. By writing $k_e = \nu$, corresponding to $Q_n = 0$, a value for the evaporation field may be calculated; the values obtained are generally within 20% of the experimentally observed values.

Although the image force theory is fairly successful in predicting the evaporation field and the majority charge species to be expected, it has defects both in its construction and in its predictions. A serious error is the use of the classical image potential in equation (1); the distance of the Schottky barrier from the surface is of the same order as the atomic radius (Muller and Tsong 1969, p. 58); at this distance from the surface the classical potential could not be expected to be correct. Indeed, the precise position of the surface is difficult to define to the accuracy which this theory assumes (Smoluchowski 1941). Secondly, no allowance is made for the short-range interatomic potentials between the evaporating atom and its neighbouring atoms, which should be taken into account in the calculation of Q_n (Brandon 1963). No allowance is made for the penetration of the field into the surface; the field will penetrate the surface for a distance comparable to the classical skin-depth $= (3/6\pi n_0 e^2)^{1/2}$ which is of the order of 0.2-0.9 Å for most metals (Friedel 1954). Various attempts have been made to include these effects, and others, such as polarization energies (Brandon 1965), (Tsong 1969, Taylor 1970, Muller and Tsong 1973) but the general form of the rate equation remains the same.

Apart from its dubious physical basis, the image force theory makes several predictions which are known to be false. Firstly the expected charge species is that species for which the evaporation field is lowest: any small difference in Q_n for two values of n will lead to a vast predominance of the species with the lowest Q_n , since $k_e(n) = \nu \exp(-Q_n/kT)$. In practice, however, it is commonly found that elements evaporate as a mixture of charge species (Brenner and McKinney 1968). Secondly, the variation in evaporation rate with field is predicted to be extremely high: rewriting equation (2) we have

$$\begin{aligned} k_e &= \nu \exp(-Q_n/kT) \\ &= \nu \exp(-(\Lambda + \sum_n I_n - n\phi)/kT) \exp\left(\left(\frac{n^3 e^3 F}{4\pi \epsilon_0 kT}\right)^{\frac{1}{2}}\right) \end{aligned}$$

The second, field-dependent, exponential is approximately $\simeq \exp(42/kT)$ for $n = 3$, $F = 4.5$ V/A, kT in eV
 $\simeq \exp(4000)$.

This term depends on $F^{\frac{1}{2}}$: a 1% variation in F will alter its value to $\sim \exp(4000 \times 1.005) = \exp(4020)$, so the evaporation rate constant k_e will vary by approximately $\exp(20) = 10^{10}$, depending on the temperature, for a 1% change in field. This is in fact much more rapid than the experimentally observed values, which lie nearer $10^{1.5}$ for a 1% change in field (Tsong and Muller 1970). A less rapid variation of k_e with F may be obtained by introducing polarization energies (Muller 1958) into equation (1);

$$Q_n = \Lambda + \sum I_n - n\phi - \left(\frac{n^3 e^3 F}{4\pi \epsilon_0}\right)^{\frac{1}{2}} + \frac{1}{2}(\alpha_a - \alpha_i)F^2 + \frac{1}{24}(\gamma_a - \gamma_i)F^4$$

where α_a, α_i and γ_a, γ_i are the polarizability and second hyperpolarizability of the atom and ion respectively. Brandon (1965) attempted to relate the bulk compressibility of the metal and the conduction

electron density to the value of α_2 which is relevant to field-evaporation; this will in general be different to that of a free atom, which is expected to have a polarizability of order 10 \AA^3 (non-SI units) (Born 1935). The polarizability will be roughly proportional to the volume of the atom or ion, and will therefore be considerably less for a multiply-charge positive ion. Brandon estimated the net polarization correction as 1-3 eV. Muller (1964) and Tsong and Muller (1970, 1971) have adopted the approach of assuming the general validity of the image potential model of field evaporation, and using it to calculate the effective polarizabilities of tungsten kink-site atoms and ad-atoms. Tsong found $\alpha = 4.6 \text{ \AA}^3$ for kink-site atoms; however, Vesely and Ehrlich (1972) found $\alpha = 4.80 \pm .03 \text{ \AA}^3$, using Tsong's data; moreover, they obtained this value using the (incorrect) assumption that tungsten evaporates as W^{2+} . When they used the correct charge, W^{3+} , they obtained $\alpha = 9.5 \text{ \AA}^3$, in marked disagreement with Tsong.

1.3.2 The Charge-Exchange Model.

An alternative approach to field-evaporation theory is the charge-exchange model (Gomer and Swanson 1963). This treats field evaporation as a continuous transition between bound metallic states and unbound ionic states, the transition occurring at the point where the energies of the states are equal.

Muller and Tsong (1973) state that the atomic potential energy

$$U_a(F,x) = - (\Lambda(F) + \frac{1}{2} \alpha_2 F^2 + 1/24 \gamma_2 F^4)$$

and the ionic energy is

$$U_i(F,x) = \sum_n I_n - \Delta E - \frac{1}{2} \Gamma - n \phi(F) - neFx - \frac{1}{2} \alpha_2 F^2 - 1/24 \gamma_2 F^4 + U_i^0(F,x)$$

$$\text{where } \phi(F) = \phi + neF/\lambda$$

$$\text{and } U_i^{\dagger}(F, x) = \sum_j \frac{K}{r_j^p(F)} - \frac{(ne)^2}{4(x + 1/\lambda)}$$

where ΔE and Γ are the energy level shift and broadening, $(1/\lambda)$ is the field penetration depth, and $U_i^{\dagger}(F, x)$ is an attempt to represent the interaction of the ion with the metal atoms as the sum of a coulomb potential and of a Lennard-Jones interatomic potential energy. They then derive the activation energy as

$$Q_n(F) = \sum_n I_n + \Lambda(F) - n\phi(F) - \Delta E - \frac{1}{2}\Gamma - neF(x + \lambda^{-1}) \\ + \frac{1}{2}(\alpha_a - \alpha_i) F^2 + 1/24(\gamma_a - \gamma_i) F^4 \\ + \sum_j \frac{K}{r_j^p(F)} - \frac{n^2 e^2}{4(x + \lambda^{-1})}$$

Although this equation may represent a better approach than the image potential model, the majority of the quantities involved are at present poorly known or impossible to calculate sufficiently accurately: for this reason the image potential model has generally been used in any attempt to correlate field-evaporation theory and experiment.

1.3.3 Ionic Tunnelling.

As Brandon (1966a) pointed out, the width of the potential barrier to field evaporation is small ($\sim 1 \text{ \AA}$); it is therefore to be expected that there will be a finite probability that an ion may tunnel through the barrier, in spite of the short wavelength of such a heavy particle. The total contribution of tunnelling to the field evaporation rate will be given by (Taylor 1970)

$$k = \sum_j \nu_r P_j D_j$$

where ν_r is a frequency factor, P_j is the probability that the

j^{th} vibrational energy level is occupied, and D_j is the probability of tunnelling from that level. We have

$$P_j = \exp(-jh\nu/kT) (1 - \exp(-h\nu/kT)),$$

and, using the WKB approximation,

$$D_j = \exp\left(-4/3 \left\{ \left(\frac{2m}{\hbar^2} \right)^{1/2} (Q_m - jh\nu)^{1/2} \right\} \left\{ \left(\frac{1}{S_m} + \frac{1}{S_v} \right) (Q_n - jh\nu) \right\}\right)$$

$$= \exp\left(-4/3 \left(\frac{2m}{\hbar^2} \right)^{1/2} \left(\frac{1}{S_m} + \frac{1}{S_v} \right) (Q_m - jh\nu)^{3/2}\right)$$

$$\text{for } jh\nu \ll Q_n \quad \text{and } D_j = 1 \quad (jh\nu \gg Q_n).$$

Here S_m and S_v are the slopes of the triangular potential barrier on the metal and vacuum sides respectively.

As discussed by Taylor (1970), Brandon (1966a) only considered the ground state. Ehrlich and Kirk (1967) put $\nu = \nu_{\text{Debye}} = k\theta_D/h$, where θ_D is the Debye temperature. Tsong (1968) used $\nu = \nu_{\text{max}}$, where ν_{max} is the bulk frequency with the highest population. Taylor states that $\nu = \nu_D$ is the better approximation, since the surface atoms are fairly well decoupled from the bulk states. The temperature below which tunnelling, rather than thermal activation over the barrier, is expected to become the dominant mechanism has been calculated as 41°K (Ehrlich and Kirk 1967) and 68°K (Tsong 1968) for tungsten; the differences are due to different assumptions about S_m and S_v . Tunnelling is expected to be essentially from the ground state at 21°K , while at 78°K terms up to $j = 7$ have to be considered. Taylor (1970) has discussed in some detail the expected sensitivity of evaporation rate to field and temperature; in general, the rates are less sensitive than those predicted

by a simple image-charge model, and correspond more closely to observed sensitivities. Tsong (1968) developed his tunnelling theory while considering the effect of temperature on the ratio of the abundances of charge species. This followed the observation by Schmidt and Vanselow (1966) that platinum evaporated as Pt^+ at 1450°K , rather than as Pt^{2+} , and by Barofsky and Muller (1968) that beryllium and copper show a rapid change in abundance between Cu^{++} and Be^{++} at low temperatures, and Cu^+ and Be^+ at higher temperatures. Tsong showed that such changes in abundance were not explicable on the thermally activated image force model, and showed that the results could be explained in terms of a tunnelling model. However, it is now known that both copper and beryllium are particularly sensitive to the influence of residual hydrogen and water vapour on their evaporation behaviour. As will be shown below, this can be true for copper even under supposedly ultra-high vacuum (UHV) conditions. Barofsky and Muller's experiments were conducted in a relatively poor vacuum, as is shown by the H^+ and H_3O^+ peaks on their published mass spectra, and it seems likely that the shift in relative abundances which they observed was due to an alteration in the products of field-induced corrosion reactions, and not necessarily to simple tunnelling. Nonetheless, it still seems likely that tunnelling should play an important role in field evaporation at the low temperatures used in field-ion microscopy, and any future theory of field evaporation must take tunnelling into account.

1.4 Field Evaporation Experiments. (Muller and Tsong 1963)

Various attempts have been made to compare field evaporation theories with experiment. Brandon (1966) measured the evaporation rates of tungsten, platinum, and molybdenum in the presence of helium, as a function of field and of temperature. He found that his data could be explained on the basis of ionic tunnelling, as described above: the tunnelling was reflected by very low apparent values for the pre-exponential frequency factor ν , which were measured as $6 \cdot 10^{10} \text{ sec}^{-1}$ for tungsten, $6 \cdot 10^6$ for platinum, and as low as $7 \cdot 10^3$ for molybdenum. He attributed the exceptionally low value for molybdenum to mechanical deformation during evaporation, (this view is tentatively supported by the work to be described below).

Following Brandon's early work, Tsong and Muller (1970) and Taylor (1970) have made direct measurements on the field evaporation rate of tungsten. Both these experimenters assumed that the presence of the helium image gas has little, if any, effect on the evaporation behaviour, following Muller and Nishikawa's statement (1964) that helium only lowered the evaporation field of tungsten by less than 2%. With the advent of the atom-probe it became clear that this lowering of the evaporation field was not due to gas impact or to electron-impact promoted evaporation, as had been suggested (Nishikawa and Muller 1964), (Young 1960). It was found (Muller et al 1969, 1970) that the atom-probe spectra contained both sharp helium and neon peaks (He^+ and Ne^+), but also peaks attributable to helium/metal and neon/metal complex ions. Although some of the initially reported complexes (Muller et al, op. cit.) were probably due to metal ions which had suffered energy losses (Chapter 2 below) or to afterpulsing in the detector and, indeed, some extravagant claims to identify with certainty

ionic species on the appearance of 1 (Muller and Tsong 1963) or 4 (Krishnaswamy and Muller 1974) ions in the mass spectrum have been made recently, there is now little doubt that many metals evaporate as helides in the presence of helium. Even the non-appearance of a helide ion in the mass spectrum is no guarantee that a short-lived intermediate helide ion might not have existed at the moment of evaporation, decaying shortly afterwards.

The formation of helide ions which are sufficiently stable to survive the 10 μ S flight time to the detector implies a fairly substantial interaction between the helium and the metal ion.

If we assume that the departing helide complex is thermally equilibrated with the specimen surface (Schulten 1973) then we may calculate a lower limit to the ion binding energy Q . The decay time will be given by

$$t = \nu^{-1} \exp (Q / kT)$$

where ν is the ionic vibration frequency. If we put $\nu = 10^{12} \text{ sec}^{-1}$, and $t = 10 \mu\text{S}$, $kT = .006 \text{ eV}$, then we obtain $Q = 0.1 \text{ eV}$. This is a minimum value since t may be considerably longer than 10 μS .

Although 0.1 eV is small compared to some of the terms in the field evaporation equations described above, it is generally agreed (Taylor 1970) that $Q_{\text{evapn.}} = 30 kT$ is a reasonable barrier to evaporation: it is thus seen that the complex binding energy is at least of the same order as the evaporation barrier. The actual binding energy of the complex ions may well be considerably higher than 0.1 eV. We may estimate the binding energy of such a complex ion by considering it as a neutral inert gas atom bound to a multiply-charged metal ion by electrostatic polarization forces, resulting from the interaction of the ion's coulomb field with the polarizable gas atom. The order of magnitude of the effect

may be calculated by considering the binding energy as

$$Q = \frac{1}{2} \alpha F^2$$

where $F = ne / (4 \pi \epsilon_0 d^2)$ is the (unperturbed)

electric field at the centre of the gas atom, α is its polarizability

and d the distance between the centres of the atom and the ion.

Taking α_{He} as 0.2 \AA^3 , $r_{\text{He}} = 1.22 \text{ \AA}$, $n = 3$, we obtain

$Q = 0.53 \text{ eV}$. This binding energy will confine the helium atom

to the immediate vicinity of the metal ion since the field F

falls rapidly with an increase in d . A more accurate calculation

should take into account the variation in field across the atom;

the polarizability of the metal ion, and the hyperpolarizability

of the gas atom, will also contribute to the binding energy,

and the overlap between the outermost orbitals of the ion and

the atom will contribute a repulsive term to the potential.

This simple model predicts that the binding energy of

metal/inert gas complex ions should be greater for gas atoms with

a high polarizability. Although the polarizabilities of the inert

gas atoms increase in the order $\alpha_{\text{He}} < \alpha_{\text{Ne}} < \alpha_{\text{Ar}} < \alpha_{\text{Kr}}$,

Muller and Tsong (1973) report finding many helium complexes,

very few neon complexes, and no argon complexes. The probable reason

for this is that the gas atom is likely to be field-ionized

by the intense electric field close to the multiply-charged

metal ion: the repulsive coulomb energy between the two resulting

positive ions will lead to the instant breakup of the complex.

For this process to occur it is necessary for the electron which

leaves the gas atom to tunnel into an empty allowed energy level.

This level need not necessarily be in the metal ion; if the complex

is very close to a metal surface, as at its moment of formation,

understanding of it; firstly, the theory had to deal

simultaneously with a number of parameters which are at present

the local field may be so modified by the presence of the metal ion that the electron can easily tunnel into the metal's conduction band. It is clear that the breakup of the complex is easiest for inert gas atoms with the lowest ionization potentials: for the noble gases, $I_{\text{He}} = 24.5$ eV, $I_{\text{Ne}} = 21.5$ eV, and $I_{\text{Ar}} = 15.7$ eV, which is at least in the correct order for the observed ionic species. Whatever the mechanisms involved in the formation and breakup of metal/gas complex ions, the effect of any imaging gas on field evaporation should not be ignored. Using the atom-probe it has been found that image gases are adsorbed on the specimen surface for considerable lengths of time (Muller et al 1969): if the image gas is pumped from the microscope, the first metal layer analysed in vacuum will evaporate at a low voltage, and will contain gas ions. The existence of this 'field-adsorbed' gas, which is bound with an energy of 0.1 eV or more (Muller et al 1969) has been explained by Tsong (1970) as due to the short-range attractive force between the gas atom, which is polarized by the applied field, and the electrical image of the induced dipole, in the metal surface. The long lifetime of this adsorbed gas film must call into question the experiments of Muller and Nishikawa (1964) who attempted to find the vacuum evaporation field of tungsten after imaging it with helium; unless special precautions are taken to remove the adsorbed helium, its presence will reduce the evaporation field in such an experiment.

1.5 Current Work.

The brier' summary of previous work on field evaporation which has been given above shows two major barriers to our better understanding of it: firstly, the theory has to deal simultaneously with a number of parameters which are at present

difficult to calculate separately; secondly, only a limited amount of experimental work directly aimed at field evaporation has been carried to completion, and almost all of this work has been done in the presence of an imaging gas. This dissertation is not directly concerned with the development of the theory of field evaporation; it is aimed at the development of experimental techniques which may be employed to establish a firm experimental basis for such a theory. The actual techniques which have been developed have been governed by the pressing need to form a firm basis from which the capabilities of the atom-probe field-ion microscope can be decided. The expanding use of the atom-probe as a routine metallurgical tool makes this experimental basis a necessity.

Chapter 2 will deal with the use of energy analysis in field ion microscopy and the selection, design, and construction of a suitable energy analyser. Chapter 3 will describe the performance of the analyser and its application to the field-adsorption of inert gases. Chapter 4 will describe the application of the analyser to field evaporation and the experimental determination of the energy spectra of metal ions evaporated under both pulsed and steady-field conditions. Chapters 5-8 will be concerned with the application of field-desorption microscopy to field-evaporation experiments. Chapter 5 will describe the construction and use of a desorption microscope to determine atom-probe aiming-errors, and the discovery of an unexpectedly finely-detailed spatial distribution of metal ions across the desorption image. Chapter 6 will describe a wide variety of experiments using the desorption microscope, including a general survey of the desorption images of most of the elements accessible to FIM. Chapter 7 will describe

the construction and use of an imaging atom-probe and its application to metallurgical problems. Chapter 8 will summarize the experimental results obtained by field-desorption microscopy and consider the modifications to field-evaporation theory necessary to account for the desorption images found. The limits of the spatial resolution of an atom-probe will be discussed.

Fig. 2.1

