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FIELD ADSORPTION AND DESORPTION OF HELIUM AND NEON

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Pulsing the atom-probe FIM in the presence of the imaging gases He or Ne reveals the adsorption of these noble gases on the surface of tips of W, Fe, Ir and Rh at temperatures as high as 78 °K. A minimum field is necessary for the adsorption; for He 2.0 V/Å is required at 21 °K and 3.3 V/Å at 78 °K, while with Ne, adsorption at 78 °K occurs between 2.3 and 5.0 V/Å only. Field desorption of the noble gas ions appears to require the simultaneous field evaporation of the tip metal atoms, which sometimes form various metal–noble gas molecular ions. The binding of the noble gas atoms is almost entirely due to the polarization energy $\frac{1}{2}\alpha F^2$. Field desorption appears possible only through the catalytic action of multiply charged metal ions. These effects suggests some reservations in the interpretation of all field evaporation data previously obtained in the presence of the image gas.

1. Introduction

The surface of the end form of a field ion microscope tip is assumed to be atomically clean, as is concluded from the well known, crystallographically perfect structures obtained with field ion micrographs of various refractory metals^{1}). The imaging gas atoms, usually helium or neon, are thought to diffuse over the surface in a hopping motion until they become ionized by transferring an electron into a protruding atom of the metal surface. It has been established that hydrogen is invisibly adsorbed between the widely spaced atoms of a seemingly clean metal surface, when it promotes field ionization of helium^{2}). Similarly, the improved imaging condition of helium-neon gas mixtures has been tentatively explained by assuming some adsorption of invisible neon, the latter acting as an intermediate collision partner in the thermal accommodation of helium^{3}). The purpose of this paper is to report in more detail^{4}) the evidence for the adsorption of both helium and neon at temperatures at least as high as 78 °K on the surface of the field ion microscope tip.

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2. The atom-probe FIM

Field ion microscopy has entered a new phase with the introduction of the atom-probe FIM[5]. This instrument (fig. 1) is based on two technical principles: by moving the emitter, the image of one surface atom, or of a very small region of the emitter, is made to fall onto a probe hole in the screen. The selected particle is field evaporated by a voltage pulse of a few nanoseconds duration superimposed on the dc imaging voltage, and is then mass analyzed by measuring its time of flight in a drift tube behind the probe hole. The time correlation between the evaporation pulse and the detection signal essentially eliminates detector noise and random image gas ions, as the instrument is gated for a few microseconds only.

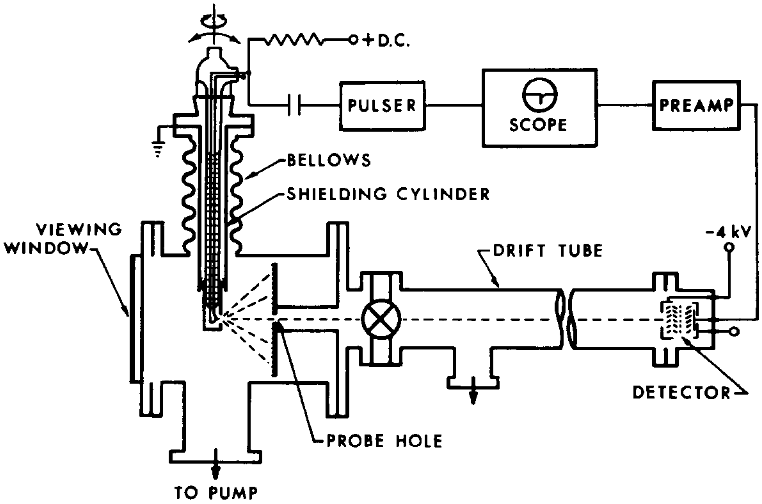

Fig. 1. Atom probe field ion microscope.

The particle's identifying mass-to-charge ratio, m/n, is calculated from the time of flight t and its kinetic energy $\frac{1}{2}mv^2$, the latter being determined by the sum of the image voltage V_{dc} and the effective pulse voltage $V_{eff} = aV_{pulse}$. The factor a, describing an over-voltage at the tip due to the transmission of the pulse on an unterminated line, and a time correction factor δ due to electronic delays between the detector and the oscilloscope readout, can be calculated[6] by using two detection spikes on one time trace obtained from single isotope tip metals such as rhodium with multiply charged ions, and adsorbed atoms such as hydrogen. If l is the length of the ion's path, measured from the tip to the detector, the observed mass-to-charge ratio is

$$\frac{m}{n} = \frac{2e}{l^2}\left(V_{\mathrm{dc}} + aV_{\mathrm{pulse}}\right)(t+\delta)^2, \tag{1}$$

where e is the electronic charge. With the present equipment the mass resolution actually obtained reaches ± 0.2 amu in the middle of the mass scale where the multiply charged ions of the heavy metals appear.

When the ion image of a selected surface region has been placed over the probe hole by adjusting the tip orientation, the field evaporation pulse may be applied after the image gas has been pumped out. However, the use of the instrument as a microanalytical tool of ultimate sensitivity for atom-by-atom analysis is much facilitated when the image gas remains in the microscope chamber. This is possible in a dynamic mode of operation when the imaging gas at a pressure of less than 0.5 m Torr is supplied to the microscope chamber while the drift tube section beyond the probe hole is differentially pumped.

The field enhanced supply rate of image gas atoms to a unit area of the tip is[7])

$$n = \frac{p}{(2\pi mkT)^{\frac{1}{2}}}\left(\frac{\pi\alpha F_0}{2kT}\right)^{\frac{1}{2}}. \tag{2}$$

Here p is the gas pressure, m the mass of the gas atom, and α its polarizability, while kT has its usual meaning. F_0 is the imaging field produced by the applied dc voltage. Eq. (2) has been derived by idealizing the tip to a sphere, and assuming a homogenous gas temperature, which is not quite true in an FIM. The effective flux of image gas to an average surface atom may be about one half of what is calculated from eq. (2) and this amounts for He at 4.5 V/Å to 3×10^4 sec^{-1}, and for Ne at 3.75 V/Å to 1.6×10^4 sec^{-1}, both at liquid hydrogen temperature, while with liquid nitrogen cooling the rates are one fourth of those. The actual ion emission from an individual surface atom may differ greatly. It depends not only upon the local supply to the site through surface diffusion, but also upon the ionization probability above the atom, which is essentially a function of the degree of protrusion of the atom.

The dc image ion current through the probe hole can be measured using the multiplier as an ion counter. At an imaging gas pressure of 5×10^{-4} Torr, sufficient to give a fairly bright helium ion image on the screen, the average time spacing between counts is much larger than the 10 or 20 μsec gating time of the oscilloscope trace. Thus, image gas ions arriving at random times are expected to show only rarely on a trace, appearing as a non-reproducible and unidentifiable mass spike.

3. Experimental results

The occurrence of mass 4 in the presence of helium and of mass 20 and 22 in the presence of neon in actual pulsing experiments is most surprising. It is clear that the gas atoms must be adsorbed at the surface to be available for desorption at the instant of the pulse. The following experimental facts have been established:

1) Adsorption of He and Ne occurs at temperatures of 21 °K as well as at 78 °K.

2) By choosing different magnitudes of V_{dc} and aV_{pulse} in such a way that their sum always gives a field high enough for field evaporation during the pulse time, one can vary the dc or holding field F_0 at the surface. It turns out that the He^+ spike appears only when $F_0 > 2.0$ V/Å at 21°K, and $F_0 > 3.3$ V/Å at 78 °K.

3) For neon, these limits are different: at 78 °K, the neon spikes appear at $2.3 < F_0 < 5.0$ V/Å.

4) Within these field ranges, the adsorption is rather independent of the tip material, as observed with W, Ir, Rh, and Fe.

5) The pulsed desorption field must be high enough to also field evaporate metal ions. He^+ and Ne^+ appear on a trace only when metal ions are observed to field evaporate through or in the immediate vicinity of the probe hole.

6) In the case of adsorbed He, the field evaporating metal ions frequently appear as ion molecules such as WHe^{+++}, WHe_2^{+++}, $IrHe_2^{+++}$ and $IrHe_2^{++}$, $RhHe^{++}$, and $FeHe^{++}$ (figs. 2 and 3).

7) Molecular ions with Ne have not yet been definitely established. They seem to occur occasionally with W, Rh and Fe, but only with an abundance of about 1% of the adsorbed neon ions.

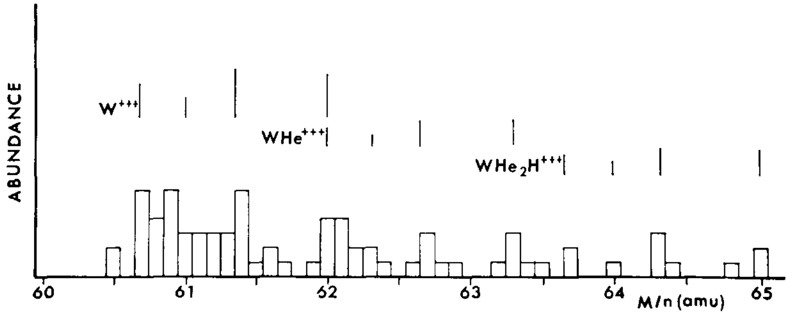

Fig. 2. Abundance of the triply charged ions of the four tungsten isotopes, and of tungsten–helium and tungsten–helium–hydrogen ion molecules at $T = 21$ °K. $P_{He} = 1 \times 10^{-4}$ Torr, $P_{H_2} < 10^{-7}$ Torr, resolution ± 0.2 amu.

8) In a mixture of helium and 20% neon, Ne^+ predominates at holding fields $F_0 < 4.5$ V/Å. At larger fields He^+ begins to show up more abundantly and is the only noble gas ion at $F > 5.0$ V/Å.

9) In the presence of hydrogen at 10^{-7} Torr partial pressure, He and Ne ions have a hydrogen atom attached on 2% of the desorbed noble gas ions. Heavy metal–helium molecular ions are also combining with hydrogen. In a helium–neon gas mixture a spike at 10 amu, with 5% abundance, could either represent Ne^{++}, or, more likely, $He_2H_2^+$.

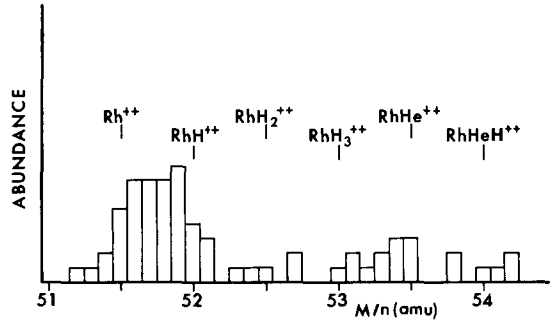

Fig. 3. Abundance of doubly charged single isotope rhodium ions, and of various metal–hydrogen and helium ion molecules, ambient same as in fig. 2.

10) At 21° K, He^+ has been field desorbed one minute after the image gas had been pumped out to 3×10^{-8} Torr, with the holding field $F_0 = 4.5$ V/Å. Thus the dwelling time of adsorbed He is at least one minute.

4. Field adsorption

These observations suggest that the adsorption is due to the electric field. Ordinarily, helium and neon are not adsorbed on metals at temperatures as high as 21 or 78°K, because their adsorption energies H_0 are only of the order of 300 and 600 cal/mol respectively[8]). In the electric field F_0, however, the energy of a particle is lowered by its polarization energy $\frac{1}{2}\alpha F_0^2$. Drechsler[9]) was the first to point out that this polarization term may be seen as a "field binding energy", adding to the normal binding energy H_0 of adsorption. Unfortunately, he applied this idea to metallic adsorbates only and obtained unrealistic numbers, such as 9 eV for tungsten at 6.0 V/Å, by using the polarizability $\alpha = 7 \times 10^{-24}$ cm^3 of the free metal atom. Actually, the adsorbed metal atom becomes a part of the surface by transferring its valence electron to the conduction band. As it is now partially shielded by the conduction electrons, its effective polarizability is very small[10]). The increase of binding energy of metal atoms due to polarization in the "low" fields used in field emission microscopy has also been noticed by Utsugi and Gomer[11]) and most recently by Klimenko and Naumovets[12]). The latter authors conclude from the undetectable contribution of polarization binding (at $F \approx 0.3$ V/Å) that the polarizability of adsorbed Na must be less than one fifth of the free atom.

With helium and neon on field ion emitter surfaces we obviously have a case of almost pure field adsorption. The polarization binding energies at $F = 4.5$ V/Å amount to 0.14 eV for He, and 0.30 eV for Ne, an order of magnitude larger than the bonds due to the van der Waals interaction. At a sufficiently high field almost every oscilloscope trace indicates a desorbed noble gas ion. Thus the average degree of coverage of the surface as determined by the ratio of the impact supply of eq. (2) and the thermal evaporation rate at the tip temperature must be of the order of one. At the limits of the fields established by the experimental observations 2 and 3 the occurrence of spikes, and hence the degree of coverage, go to zero. The adsorption time τ in the field F is expected to be

$$\tau = \tau_0 \exp\left(\frac{H_f}{kT}\right) = \tau_0 \exp\left(\frac{H_0 + \frac{1}{2}\alpha F_0^2}{kT}\right), \tag{3}$$

and a numerical calculation, assuming $\tau_0 = 10^{-12}$ sec, gives reasonable dwelling times τ, between 10^{-3} and 10^{-6} sec, for the experimental limiting fields given above (fig. 4).

The upper field limit of 5.0 V/Å for the occurrence of adsorbed neon is probably due to the inability of the gas to reach the emitter surface beyond

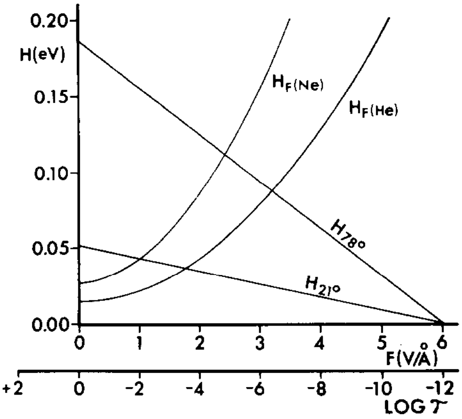

Fig. 4. Adsorption energy H_f for helium and neon as a function of field, and evaporation energy H as a function of adsorption time for 21 °K and 78 °K.

that field[3]). All neon atoms are ionized in the space above the surface on their approach.

The disappearance below 4.5 to 5 V/Å of adsorbed He in He–Ne mixtures may be due to the inability of helium to build up a sufficient degree of coverage under the impact of the more energetic, polarized neon atoms.

5. Field desorption

The mechanism of field desorption of the adsorbed noble gas atoms poses a particular problem. The image force theory of field desorption[13]) predicts a desorption field at zero temperature

$$F = e^{-3}(H_0 + I - \phi)^2, \tag{4}$$

where I is the ionization energy of the gas atom, and ϕ the work function of the metal surface. While this equation gives good data for metal atoms field evaporating with a single charge, it predicts unreasonably high fields of 28 and 20 V/Å for He and Ne. As Gomer[14]) has pointed out, in the case of large ionization energies eq. (4) should be replaced by

$$F = \frac{H_\mathrm{f} + I - \phi}{ex_\mathrm{c}} \tag{5}$$

Here x_c is the critical distance from the surface where the atomic potential curve intersects the ionic potential curve. Rather than calculating F we might take the experimental value, 6.0 V/Å in the case of helium or neon field desorbing from tungsten, and thus require critical distances $x_\mathrm{c} = 3.3$ Å for He and 2.8 Å for Ne. It is hard to imagine how the field adsorbed gas atoms could get that far above the surface without an appreciable activation energy. The impact of another image gas atom is a too rare event to be occurring during the nanosecond pulse time. We must conclude that it seems impossible to field desorb helium and neon from a metal surface without the assistance of some catalytic action.

The observations 5, 6 and 7 indicate that a promotion of the field desorption process is actually occurring. The simultaneous field evaporation of metal ions from the surface seems to be a prerequisite for the desorption of the noble gas ions. No ions are desorbed when the central regions of the (011) and (112) planes of tungsten or the (001) and (113) planes of rhodium are placed over the probe hole and then pulsed, until the receding net plane edge reaches the probe hole. Occasionally there are traces containing only one He^+ or Ne^+ ion; the metal ion seen evaporating nearby must have missed the probe hole or the detector.

6. Conclusion

The experiments reported here are of an exploratory nature, and need be extended in various directions. No use has been made of the capability of the atom-probe FIM to localize the origin of the desorbed particle within the atomic resolution limit of the instrument. The field adsorbed noble gas atoms have been taken from the edges or the vicinity of the (011) and the (112) plane of the bcc metals, W and Fe, and from areas near the (001), (102) and (113) planes of the fcc specimens, Ir and Rh. It is well possible that the critical field ranges as well as the nature and relative abundance of the metal-noble gas molecular ions may vary with the crystallographic sites. The occasional formation of HeH^+, HeH_2^+, He_2H^+ and NeH^+ ions in the presence of a partial pressure of 10^{-7} Torr H_2 which has also been observed in these experiments needs to be more thoroughly investigated. Besides the metal hydride ions already known[15]), the observation of $m/n = 54$ and 54.5 with rhodium points to ion molecules Rh HeH^{++} and Rh HeH_2^{++}, and similar, triply charged molecule ions are found with tungsten (figs. 2 and 3).

The knowledge of the abundant presence of field adsorbed helium and neon under the ordinary imaging conditions of the FIM may not have a direct bearing on the interpretation of images, as the adsorbates carry very little positive charge and are therefore invisible. The so far unexplained lower contrast of the neon ion image, compared to the helium ion image of the same surface, may be better understood by the presence of the larger, adsorbed neon atoms in the interspaces. It is also no longer necessary to assume a very small thermal accommodation coefficient for the incoming gas atoms, as they will collide efficiently with the adsorbates rather than with the heavy metal atoms only. The number of hops required for accommodation will now be much smaller than has been assumed previously[16]). Many, if not most of the imaging ions may originate by field ionization after some time of adsorption and after having been brought up to the critical distance by a collision with a newly impinging gas atom.

While the involvement of the field adsorption phase of the imaging gas seems not to affect any earlier conclusions about the imaging process, more serious thought will have to be given to the interpretation of measurements of field evaporation of metals in the presence of the image gas. The reduction of the evaporation field[3]), which was found to be too high to be explained as direct energy transfer from impinging gas molecules[17]), can now be explained by the impact of the imaging gas atom on a surface metal atom whose binding energy has been reduced by the adjacently adsorbed image gas. The determinations of surface binding energies from experiments in which single metal atoms are planted on the field ion microscope tip and then field evaporated in the presence of adsorbed image gases[17-19]) will need a careful reconsideration after the field evaporation products, multiply charged metal ions as well as metal-noble gas molecular ions, have been definitely established with an atom-probe FIM.

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