Field desorption of helium and neon from tungsten and iridium*

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The first complete crystallographic distribution of helium and neon field adsorbed on tungsten and iridium surfaces has been determined using field desorption mass spectrometry. At 80 K He\(^+\) is removed from tungsten at high work function areas. The absence of He\(^+\) in other regions indicates that either helium is not adsorbed, or that it is removed from the surface as a WHe\(^3+\) molecular ion during field evaporation of the substrate which is required for He\(^+\) detection. Helium adsorbed on iridium at 80 K may form IrHe\(^3+\) and neon IrNe\(^2+\) near prominent zone lines. The absence of ion species in specific crystallographic regions of iridium and tungsten suggests that when interpreting atom probe results in certain metallurgical applications.

**INTRODUCTION**

The presence of noble gas atoms adsorbed on field-ion emitter surfaces has been clearly established by a number of previous investigations.\(^1,2\) Both theoretical\(^3\) and experimental\(^4\) considerations have localized the position of the noble-gas adsorbate to the apex of each protruding kink-site atom and have identified the adsorption process with a field-induced dipole–dipole interaction. Of particular interest has been the interaction of the inert gas species with its corresponding substrate atom to produce a stable molecular ion,\(^5\) whose appearance can depend on the substrate temperature and the particular crystal region selected for observation.\(^6\)

In this paper we extend the observations of noble-gas adsorption by presenting complete crystallographic distributions of helium and neon adsorbed on tungsten and iridium surfaces and demonstrate how such distributions can reflect the existence of stable molecular ion species. We further suggest that the absence of detected species in specific crystallographic regions may indicate an inhomogeneous ion production at the surface, an effect which must be considered when using the atom-probe in metallurgical applications.

**APPARATUS**

The ultrahigh-vacuum field-desorption spectrometer used for this study is identical to the one presented previously\(^7\) except that the specimen is both biased and pulsed to eliminate any ambiguity resulting from electron-optical considerations.\(^8\) Crystallographic distributions are obtained by activating the spherical channel electron multiplier array (CEMA) detector coincidently with the arrival of a preselected field-desorbed species and photographically recording the resulting image. By maintaining a very low-evaporation rate (10–100 ions per pulse) and photographically integrating 100 or more evaporation events, a species distribution is obtained which is statistically significant and not influenced by possible trajectory variations resulting from the high ion densities and large changes in surface geometry which accompany large evaporation rates.

Mass resolution and, therefore, the ability to separate adjacent species is essentially determined by the width of the CEMA gate pulse, which in this study, was 28 nsec. Although this is more than sufficient to separate at typical operating potentials He\(^+\) (140 nsec) from...
Ne\(^+\) (314 nsec) or substrate species, it is not sufficient to unambiguously separate molecular ions from substrate species. Nevertheless, the presence and crystallographic distribution of molecular ions can be deduced by field evaporating the substrate and comparing the resulting inert gas and substrate-desorption micrographs, if one assumes that the inert gas species is adsorbed at all kink-site locations on the surface. The argument is as follows: Since the adsorption of inert gas is owed to a dipole-dipole interaction with the polarized surface atom one would expect that each kink-site atom would eventually adsorb a noble gas species, even in regions of relatively low field. If the substrate is evaporated at a very low rate so that only protruding atoms have a high probability of removal, each kink-site atom will be removed along with its adsorbed inert gas atom as a distinct species or in association with its inert-gas atom as a complex molecular ion. Provided this evaporation rate is maintained during many successive pulses, and the time between pulses made long enough to assure inert gas adsorption at all kink-site locations, the total number of substrate species removed will always equal the number of inert gas species removed, with some inert gas retaining its identity as a distinct species and the rest forming molecules with the substrate. However, because of the width of the gate pulse applied to the detector, the substrate and molecular species cannot be resolved and will appear on the same micrograph. But in regions where molecules are formed, no distinct inert-gas species will be present so that in the inert-gas micrograph regions associated with stable molecular-ion formation will appear dark. Therefore, we will use the following hypothesis in analyzing our data. Dark regions of the inert gas micrograph which correspond to bright regions in the substrate micrograph indicate areas of stable molecular-ion formation.

DISCUSSION

Figure 1 is a gated desorption micrograph of He\(^+\) from a (111) oriented tungsten specimen whose corresponding W\(^{10}\) distribution is shown in Fig. 2. A comparison of the micrographs indicates three distinct crystallographic regions of interest, summarized schematically in Fig. 3. First, the relatively low field (110), (101), and (011) regions as well as the vicinity of the zone lines between these regions and the center of the (111) plane are areas in which the probability of formation, and stability, of WHe\(^{10}\) is very high. The relatively few He\(^+\) image spots present in these areas indicate that the probability of formation of a stable molecular-ion species is not 100% but is greater than 85%.

Second, the (111) region as well as the zone lines between the (111) and (211), (112), and (121) planes are areas in which there is only a small probability of finding either W\(^{10}\) or He\(^+\). Figure 4, which is a desorption micrograph of Ne\(^+\), further indicates that the probability of finding Ne\(^+\) in these regions is small. These areas of low-relative-ion yield will be considered later.
The remaining imaged area shows W^+\text{ and } \text{Ne}^+\text{, and Ne}^+\text{ and therefore indicates that molecular ion formation in these regions is not probable, or that the probability of dissociating the molecular species is high.}

At 300 K the distribution of W^+ shows the same dark regions of Fig. 2 taken at 80 K, but \text{He}^+\text{ and } \text{Ne}^+\text{ are not observed in detectable amounts, so that molecular species are not expected to be present. At 21 K, \text{He}^+\text{ is observed on (110)-like planes with high probability, exactly opposite to the 80 K observation of Fig. 1. This suggests that the formation or stability of the molecular species in these regions below 80 K is also negligible.}

These observations support the conclusions of an earlier atom-probe examination, in which the crystallographic distribution, stability, and temperature dependence of WHe^+ was discussed.

Figures 5 and 6 show the crystallographic distributions of Ir^+\text{ and } \text{I}^++\text{, and Figs. 7 and 8 the corresponding } \text{He}^+\text{ and } \text{Ne}^+\text{ distributions. A comparison of these figures indicates two main features of interest. First, the vicinity of the zone lines extending from the central (111) plane may be areas in which the formation of stable IrHe^+ and IrNe^+ is highly probable. Unfortunately, the distribution of these species cannot be examined directly since the former is separated by only 6 nsec from the substrate species and the latter by 33 nsec, which is within the present gate position uncertainty of \pm 5 nsec. It is probably that these highly localized species have been overlooked in previous high-resolution atom-probe investigations because this technique requires precise positioning of a small probe hole for species detection.}

Second, there are dark regions which are coincident in the Ir^+, \text{Ir}^+, \text{He}^+, \text{and Ne}^+ micrographs again indicating specific regions of the surface having low relative-ionic yield. As in the case of tungsten, these regions are retained at 300 K and at 80 K even in the presence of \text{7}\times\text{10}^{-7} \text{ Torr of helium. Such dark regions have also been seen in nanogated desorption images of Pt^+\text{ and } \text{W}^+\text{ and } \text{appear to be characteristic of the metals used in field-ion microscopy. Although the low ion yield in these regions may be explainable in terms of simple trajectory or magnification considerations, or require a more unorthodox explanation such as ion neutralization at the surface, it must be considered in all atom-probe determinations of species distribution. The atom-probe technique relies, for positioning its small probe hole, on an inert-gas ion image which does not directly indicate regions of low ion yield. Although not previously appreciated, it is apparent that the variation in detected ion yield over the surface, which appears to be independent of the actual species distribution either adsorbed on the surface or distributed in the bulk, can significantly alter absolute compositional profile interpretations. The clue to possible problem regions, when using the atom probe, is an area of increased regional brightness in the ion image which seems, at least for the metals we have examined, to be uniquely associated with areas of low ion yield during desorption.}

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**Figures:**

- **Fig. 7.** Integrated desorption image of \text{He}^+\text{ on (111) iridium. 10 events/100 sec, } p=2\times\text{10}^{-7} \text{ Torr Ne, } T=80 \text{ K.}
- **Fig. 8.** Integrated desorption image of \text{Ne}^+\text{ on (111) iridium. 10 events/100 sec, } p=2\times\text{10}^{-7} \text{ Torr Ne, } T=80 \text{ K.}

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**References:**

- Müller, E. W., 13th Field Emission Symposium, Bonn, Germany, 1968.
- Müller, E. W., private communication.
- Panitz, J. A., Seminar at the National Bureau of Standards, Gaithersburg, Maryland, 1974. The origin of the low ion yields will be discussed in detail in a future publication.
- To minimize this difficulty, one should always measure the relative abundance of substrate- and impurity- or substrate and adsorbate as a function of crystallographic orientation.