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7/25/68
FIELD-ION MICROSCOPE STUDIES ON SURFACE PROPERTIES OF TITANIUM

A THESIS
Presented to
The Faculty of the Graduate Division
by
Rajinder Kumar

In Partial Fulfillment
of the requirements for the Degree
Master of Science in Metallurgy

Georgia Institute of Technology
June, 1971
FIELD-ION MICROSCOPE STUDIES ON SURFACE PROPERTIES
OF TITANIUM

Approved:

Chairman:

Date approved by Chairman: 5/18/71
ACKNOWLEDGMENTS

The author is very grateful to Dr. H. E. Grenga, whose invaluable guidance and advice contributed very largely to the successful completion of this thesis. The author wishes to express thanks to Dr. R. F. Hochman and Dr. B. G. LeFevre for reviewing this work.

The encouragement and understanding expressed by the author's parents, Mr. and Mrs. R. K. Aggarwal, are deeply appreciated. The author thanks all his colleagues who rendered help at all times.

The author wishes to acknowledge the aid of the AFOSR (Project Themis Contract No. F-44620-68-C-0008) for support of this work. Partial support by Advanced Research Projects Agency (ARPA Order No. 878) is also acknowledged.
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SUMMARY

The purpose of this study was to investigate surface properties of titanium with particular interest in the interaction of titanium with hydrogen and the contribution of hydrogen in lowering the interplanar binding strength of the specific planes of titanium. The results of this study along with the previous studies on hydrides can be helpful in establishing the stress-corrosion mechanism in titanium. During the course of the experiments the nature of surface oxides on titanium was also revealed. While the proper technique for successful helium-ion microscopy was obtained in the later stages of this work, it was found that hydrogen-ion microscopy yielded much of the desired information on the hydrogen interaction with titanium surfaces.

Hydrogen-ion microscopy of titanium does not give atomic resolution, but does distinctly reveal the crystallographic regions on the surface. Surface films on titanium specimens were removed by field evaporation. The end form of titanium in hydrogen-ion microscopy, when compared to that in helium-ion microscopy, represents the effect of hydrogen on the binding energy of titanium at high field. The observed preferential evaporation in hydrogen of the \{10\overline{1}1\} and \{0001\} planes of titanium is attributed to the lowering of interplanar binding or surface energy of these planes at high field. The results on thermal faceting in hydrogen in the absence of field indicate that the lowering of surface energy of these planes is due primarily to the hydrogen interaction. The previously observed cleavage planes, \{10\overline{1}7\} or \{10\overline{1}8\} during
stress-corrosion cracking of titanium alloys can be represented by a combination of cleavage along the \{10\overline{1}\} and \{0001\} planes. It is therefore proposed that the effect of hydrogen on the interplanar binding strength must be considered along with the previously proposed hydrides in ascertaining the role of hydrogen in stress-corrosion mechanism.
CHAPTER I

INTRODUCTION

Titanium and its alloys have an excellent strength to weight ratio along with good general corrosion resistance. These qualities make them suitable structural materials for aerospace and other industries. The influence of environment on the mechanical properties of these materials is very critical. In stress-corrosion cracking certain corrosive environments cause these alloys to fail in a brittle manner at stresses lower than those required for ductile fracture in air.

The stress-corrosion cracking of alloys is a complex process dependent upon both metallurgical and environmental variables. In many hydrogen-containing environments the stress-corrosion cracking of titanium alloys has been attributed to a form of hydrogen embrittlement, but the exact role of hydrogen in the embrittlement mechanism is not yet clear. The embrittlement of titanium by hydrogen may be the result of one or more of the following: a) precipitation of hydrides, b) hydrogen segregation at defects or c) some other mechanism involving external or internal hydrogen. For example, a lowering of the surface energy or the cohesive strength of titanium by adsorbed or absorbed hydrogen. The interaction of hydrogen with titanium and the possible role of hydrogen in SCC mechanisms are briefly reviewed in the literature survey.

The purpose of this thesis is to study the interaction of hydrogen with titanium and the effect of hydrogen on the surface energy at
high fields. While hydrides can generally be observed by optical or electron microscopy, the observation of very thin hydrides or hydrogen segregation requires higher magnification and resolution than afforded by these techniques. Furthermore, in order to study the interaction of hydrogen with titanium and the effect of hydrogen on the surface energy, clean surfaces of known orientation are required. Both high magnification and resolution as well as an approach to clean surfaces can be obtained with field-ion microscopy techniques. The nature of the surface films can also be studied in the field-ion microscope. Therefore, field-ion microscopy was chosen for these studies, and the pertinent literature on these techniques is also reviewed.
CHAPTER II

LITERATURE SURVEY

A. Interaction of Titanium With Hydrogen

1. Solubility of Hydrogen

The titanium-hydrogen phase diagram from approximately 300°C to 1000°C for hydrogen at one atmosphere pressure has been reported by McQuillan (1). From this phase diagram and additional data on the solubility at lower temperatures by Lenning, et al. (2), it is found that the solubility of hydrogen in alpha-titanium decreases sharply with decreasing temperature, from 7.9 atomic percent or 1680 ppm at 300°C to 0.1 atomic percent or 20 ppm at room temperature. The solubility in the beta-phase is considerably higher. Hydrogen is generally assumed to occupy the octahedral sites in the alpha-titanium lattice (3). This is because the hydrogen atom which has a radius of 0.41 Å can be accommodated more readily by the octahedral site (0.62 Å radius) than by the smaller tetrahedral site (0.343 Å radius).

Titanium absorbs hydrogen by reaction with molecular hydrogen, ammonia, hydrocarbons, water vapors or other hydrogen containing substances. The corrosion of titanium is generally accompanied by hydrogen absorption (4).

A study of several factors affecting the reaction between titanium and hydrogen gas has been conducted by Williams, et al. (5). The presence of an oxide film on titanium acts as a barrier to hydrogen absorption at low temperatures. Galling or abrasion of the surface or vacuum
annealing to dissolve the surface film increases hydrogen absorption. The interaction is also favored when ultra high purity hydrogen is used. It was also reported that alpha-beta or beta titanium alloys appear to react more rapidly and absorb larger quantities of hydrogen than alpha alloys.

There appears to be some controversy in the literature regarding the influence of interstitials, such as oxygen and nitrogen, on the solubility of hydrogen in titanium. The solubility of hydrogen in titanium specimens containing 0.2 weight percent oxygen and 0.2 weight percent nitrogen was measured by Lenning, et al. (6). In this study hydrogenated specimens were annealed at 400°C for 64 hours, cooled to the required temperature, held at this temperature for 20 hours, and then water quenched. The hydrogen content of the specimens was determined and solubility curves were plotted from 300°C to room temperature. These solubility curves indicated that neither oxygen nor nitrogen has any appreciable influence on the solubility of hydrogen in titanium at room temperature. At temperatures above 75°C, however, both of these elements appear to increase the hydrogen solubility by approximately 200 ppm. Kolachev, however, has reported (7) that oxygen and nitrogen interstitials "expel the hydrogen from titanium and increase its equilibrium pressure above the metal." Also, Gibb and Kruschwitz reported (8) that traces of oxygen and nitrogen retard the attainment of equilibrium between titanium and hydrogen and generally displace it in the direction of lower hydrogen content.

The addition of 10 weight percent tin to titanium increases the apparent hydrogen solubility in alpha-titanium. For example, at room
temperature the hydrogen solubility in this alloy is approximately 50-100 ppm (6). The addition of five weight percent aluminum also increases the apparent solubility of hydrogen in alpha-titanium (7). As pointed out in the next section, however, the apparent increase in the hydrogen solubility in titanium-aluminum alloys may be due to an increase in activation energy for hydride precipitation rather than an actual increase in equilibrium solubility of hydrogen.

2. Hydrides

When the hydrogen content of titanium exceeds a critical value, the precipitation of hydrides occurs. The critical hydrogen concentration for hydride precipitation in pure titanium at room temperature has been reported to be 80 ppm (9). The addition of aluminum to titanium increases the critical concentration for hydride precipitation at room temperature; for example, in Ti-5Al alloy this value is reportedly 180 ppm (9), in Ti-8Al, 450 ppm (9), and in Ti-8Al-1Mo-1V alloy, 800 ppm (10). The increased hydrogen concentration required for hydride precipitation in Ti-Al alloys was initially attributed to increased equilibrium solubility of hydrogen in these alloys. Boyd (10), however, has recently proposed that the solubility of hydrogen in alpha-titanium is not appreciably affected by the addition of aluminum, but these alloys can be supersaturated in hydrogen as aluminum increases the activation energy for hydride nucleation.

Boyd's proposal is based on his observations of hydride precipitation in the Ti-8Al-1Mo-1V alloy. When the critical concentration of hydrogen (800 ppm) was exceeded slightly, a large volume fraction of hydride precipitated spontaneously. If 800 ppm were the equilibrium
concentration of hydrogen only small amounts of hydride should precipitate as the critical concentration was increased slightly above this value. Boyd also estimated the volume fraction of hydride formed and concluded that almost all of the available hydrogen in the alpha titanium matrix was consumed during the precipitation.

Additional observations by Boyd on strain induced hydrides in the Ti-8Al-1Mo-1V alloy further supported his proposal that the activation energy for hydride precipitation was increased by the presence of aluminum. During deformation at room temperature, thin hydrides were formed in these alloys containing only 200-600 ppm of hydrogen. The strain induced hydrides had a BCC structure and were formed in the (1010) slip bands. The lattice parameters of the BCC hydride were closer to those of the Ti-Al matrix than were those of the normal gamma-hydrides, thereby decreasing the activation energy for hydride precipitation.

Louthan (11) investigated the stress-orientation of gamma-hydrides in A-70 titanium. The specimens were hydrided at 450°C and slowly cooled to room temperature. These specimens were then solution treated at 425°C for 5-16 hours and loaded to a tensile stress of 0, 15000 and 30000 psi. The specimens were held at 425°C for two hours before cooling to room temperature while under stress. The specimens cooled under stress of 0 or 15000 psi contained randomly oriented hydrides. In the specimens cooled under stress of 30000 psi, however, the hydrides precipitated on the titanium habit planes most nearly perpendicular to the stress axis. Louthan pointed out that the precipitation of hydrides caused expansion perpendicular to the habit plane or in a direction that tended to relieve the applied stress. The hydride platelets produced under stress were found to be on the (1010) and (1011) planes.
B. Possible Role of Hydrogen in Stress-Corrosion Cracking Mechanisms

The stress-corrosion cracking phenomena of titanium and its alloys in hydrogen containing environments such as water, methanol and aqueous solutions has been explained as a form of hydrogen embrittlement. Initially it was proposed that the embrittlement resulted from precipitation of hydride in the matrix (10, 12-14). The hydride precipitation may favor cleavage crack propagation in the plastic zone immediately ahead of it. If the hydride is stress oriented, then the increase in precipitate volume also may generate triaxial stress conditions promoting cleavage. This would cause brittle fracture at lower stress levels. In SCC investigations, however, the hydride phase has not yet been detected on the fractured surfaces (15). This led Powell and Scully (15) to suggest that either the hydrides were too thin to be detected even by transmission electron microscopy or that preferential segregation of hydrogen occurred along some defects. Burte (16) had previously proposed that hydrogen atoms segregate to lattice defects such as dislocations, vacancies or grain boundaries, prior to hydride nucleation. Powell and Scully (15) suggested that the formation of a few layers of the hydride structure on slip systems of titanium lattice would provide substantial barrier to dislocation movement, particularly in the susceptible alloys in which cross slip is not an easy process.

Another factor which should be considered in the assessment of the role of hydrogen in stress-corrosion cracking is the effect of absorbed or adsorbed hydrogen on the surface energy or the cohesive strength of titanium and its alloys. If the surface energy is lowered
by hydrogen, then effectively the interplanar binding energy or brittle fracture stress would also be lowered. The surface energy changes associated with gas adsorption are very specific; an example is given by the work of Brenner using field-ion microscopy. This work is reviewed in the next section II-C-3. The present author suggests that lowering of surface energy of the cracked surface by adsorbed hydrogen may decrease the interplanar binding energy of a few atomic layers ahead of the crack tip and thus lower the brittle fracture stress. If internally absorbed hydrogen is also involved in the mechanism, the absorbed hydrogen may lower the cohesive strength of titanium along certain crystal planes and hence decrease the brittle fracture stress. The increased hydrogen content in Ti-Al alloys may aid such a mechanism. Therefore, it is proposed that the role of hydrogen in lowering the surface energy and cohesive strength should not be ignored in the mechanism of stress-corrosion cracking; the present thesis investigates the effect of hydrogen on the binding energy of titanium.

C. Field-Ion Microscopy

The field-ion microscope is the only microscopical device powerful enough to display directly the atomic arrangement at the surface of metals. The importance of this tool stems from the resolution of 2-3 Å and the high magnification of approximately one million diameters. In field-ion microscopy a wire specimen with a radius of curvature of only a few hundred angstroms is used. This is required to obtain the high field (300-450 mv/cm) on the tip of the specimen to ionize helium or other gases used in the imaging process. The specimens are prepared electrolytically. The principle, experimental aspects and limitations
Field-ion and field-emission techniques have important applications in studying the surface and bulk characteristics of metals. The field-ion technique reveals the atomic arrangement at the surface, whereas the field-emission technique investigates the electronic structure of the surface. Frequently, a combination of both these techniques leads to more useful data. The surface properties studied so far by these techniques include surface mobility, surface corrosion and vapor deposition. Chemisorption studies by these techniques reveal the complexity of this phenomena at an atomic level (21-24).

In this review emphasis will be on surface stresses due to high electric fields and the field evaporation process in the presence of reactive gases. These aspects are essential because the results of this work are interpreted in terms of them. In the latter portion of this review the field-ion microscopic observations on faceting due to heating specimens in gases and the field-ion microscopy of hexagonal metals is summarized.

1. Field Stress

A large amount of mechanical stress is exerted on the conductive surface due to electric potential. The regions under stress become more susceptible to gas interactions and may become weak. The magnitude of stress developed is governed by the following equation (20).

\[ \sigma = \frac{F^2}{8\pi} \]

where \( \sigma \) = stress in dynes/cm\(^2\) and 
\( F \) = field on the tip in e.s.u.
At the ionization potential of hydrogen (228 mV/cm$^2$) the amount of stress is of the order of $5 \times 10^{10}$ dynes/cm$^2$, whereas at the ionization potential of helium (370 mV/cm$^2$) the stress is of the order of $1 \times 10^{11}$ dynes/cm$^2$ (20). These stresses act on the surface and may leave all the atoms on the surface in metastable positions. The degree of shift of these atoms from equilibrium position depends upon the local field strength and is maximum at the apex of the field-ion specimen. The shear component of this stress, because the surface is not hemispherical, causes dislocations to move and sometimes the specimen to fracture. The interatomic distances on the surface layers are also changed to some extent and a large number of defect sites are created due to this field stress (25).

2. Field Evaporation

The atomic structure of the surface as seen in the field-ion image depends upon the evaporation process (26,27). As the applied field is increased above the best image field, the metal atoms are evaporated from the surface. The applied potential at which the atoms are removed from the surface is called the field evaporation voltage. Details of the field evaporation process are available in the literature (17-19, 26, 27).

The following equation can be derived by considering the image force theory of field evaporation of a clean metal (17).

$$F = (ne)^{-3} \left[ \lambda + I_n - n \epsilon + \frac{1}{2} (\alpha_a - \alpha_i) F^2 - kT \ln \frac{t}{t_0} \right]$$

where $F$ = field strength for evaporation
ne = charge on the evaporated metal ion ($n = 1, 2, \ldots$)
\( \lambda \) = vaporization energy of the metal atom at the kink site

\( I_n \) = \( n \)th ionization energy of metal atom

\( \phi \) = work function of specific crystal plane

\( \alpha_a \) = polarizability of the metal atom at the surface site

\( \alpha_i \) = polarizability of the free metal ion

\( k \) = Boltzmann's constant

\( T \) = absolute temperature

\( t \) = time required for evaporation

\( t_o \) = vibration time of the bound surface atom.

Müller (25) has reported the effect of polarization, field stress and image gas impact on the field evaporated end forms. He proposes that the end form is established by balancing the local field at the evaporation site with the binding energy of the evaporating metal atom. A considerable part of this energy may be due to polarization which can be described by field penetration. The field evaporated end form is further modified by the presence of the image gas when molecules effectively transfer their dipole attraction energy in the collision with the surface.

The effect of hydrogen promotion on field evaporation has been discussed by Müller (28). Of the metals molybdenum, tungsten, iridium and platinum (29), platinum is more sensitive to hydrogen. At 73-75 percent of the best helium image voltage, hydrogen corrodes the whole surface displacing surface atoms and creating irregular net plane edges and surface vacancies. The corroding effect is related to the field induced chemical reaction. A mechanism by which hydrogen can reach the tip surface has been proposed by Nishikawa and Müller (29). They
propose that migration of hydrogen on the surface from the shank towards
the tip takes place during imaging when hydrogen promotion is used.

Products of hydrogen promoted field evaporation in the case of silicon
and copper are their respective metal-hydrogen complex ions (30).

The presence of a chemisorbed layer modifies the field evaporation
process (22). Since the chemisorbed gases can influence the physical
properties (thermal and electrical conductivities, surface structure
etc.,) therefore the properties of chemisorbed layer differ significantly
from that of the bulk metal. It is suggested that the chemisorbed
layer is less strongly bound to the rest of the metal, i.e. the bonds
linking the surface atoms with their neighbors in and below the surface
are weakened. In other words the interplanar binding strength is lowered
due to chemisorption. The field evaporated particles are not metal ions
but are metal-gas complex ions with charge n'e. In terms of the equa-
tion for field evaporation this effect of chemisorption is expressed by
a decrease of vaporization energy of metal atom λ to λ - Δλ and increase
in the work function from φ to φ + Δφ; however, the work function contribu-
tion is very small compared to vaporization energy. Therefore in the
presence of an active gas the equation for field evaporation is modified
as follows:

\[ F' = (n'e^{-3} e^{-3})[λ - Δλ + I_{n'} - n'(φ + Δφ) + \frac{1}{2}(ω_a - ω_i)F'^2] - kTln\frac{β}{\mathcal{E}_0} \]

where \( F' \) = field strength for evaporation in presence of an active gas
\( n'e \) = charge on the evaporated metal gas complex ion
\( I_{n'} \) = n'th ionization energy of the metal gas complex ion
\( Δφ \) = change in work function due to chemisorption and
\[ \Delta \lambda = \text{change in vaporization energy due to chemisorption.} \]

The influence of a chemisorbed substance on field-ion microscope specimens has been referred to as "gas etching or gas promoted field evaporation" (23). The degree of interaction due to adsorbate varies on different crystallographic planes. Facets develop in those regions where the interaction is greater. Three types of interactions have been reported by Rendulic (23):

(i) The adsorbate does not cover the entire surface, then the covered areas are preferentially evaporated.

(ii) When the adsorbate covers the whole surface, the type and rate of interaction with different crystallographic planes varies. Therefore some planes where the interaction is greater will field evaporate at lower field than others.

(iii) In the regions of low electric field, the combined effect of the adsorbate and the electric field is not able to move some surface atoms into energetically more favorable positions. The result is an irregular appearance of the surface with facets in some regions.

When the adsorbate covers the whole surface, a few planes evaporate at lower field than others and develop flats, i.e. locally higher radii of curvature. The evaporation at low field strength means that these planes bind chemisorbed substances more strongly. According to the present author this is analogous to saying that the interplanar binding energy or surface energy is lowered preferentially on certain planes due to gas adsorption.

3. Facets on FIM Specimens Due to Heating in Gases

S. S. Brenner (31,32) has reported the changes in surface energy
and facets on tungsten and iridium specimens which were heated in vacuum or in the presence of oxygen and carbon monoxide. He reported that the gaseous impurities can either lower or raise the rate of faceting depending upon their nature. On heating in vacuum of less than \(10^{-9}\) torr, iridium developed flats on the \{111\}, \{100\} and \{012\} orientations. In the presence of \(10^{-3}\) torr oxygen, the \{012\} flats did not form but the enlargement of troughs containing the \{110\} and \{113\} planes was very prominent. In another experiment where iridium was heated in carbon monoxide and oxygen mixtures, the results showed that for 50 percent carbon monoxide content in the gas mixture the \{012\} flats were very prominent compared to \{113\} flats. As the carbon monoxide content was decreased the prominence of \{113\} flats, due to higher oxygen adsorption, increased. When the carbon monoxide gas content in the mixture was 25 percent, the size of \{012\} and \{113\} facets was almost equal. Further decreasing the carbon monoxide content to 13 percent caused disappearance of the \{012\} facets. From these results Brenner concluded that the free energy was appreciably reduced on \{113\} planes due to oxygen adsorption and on the \{012\} planes due to carbon monoxide adsorption. Therefore, it is seen that the gas effect is very specific and varies from one crystallographic plane to another. Hence gas adsorption has a very profound effect on the surface energy and can even change the order of decreasing surface energy of the planes from that for the clean metal. Therefore, the order of decreasing surface energy of the planes depends not only on the metal, but also on the gas environment.

4. Field-Ion Microscopy of Hexagonal Metals

Field-ion images of ruthenium, rhenium (33,34), hafnium (35) and
cobalt (36) have been reported. A detailed explanation of the field evaporated end forms of hexagonal metals has also been reported.

Table 1 compares the various properties of hexagonal metals which give rise to image differences (33). Field ion images of titanium and ordered Ti$_3$Al have also been given by Grenga and Hochman (37). These initial images, however, contained a high concentration of impurities.

The relatively bright area around $\{11\bar{2}0\}$ planes is characteristic of all hexagonal metals studied so far. The typical bright area around $\{11\bar{2}0\}$ planes may result from differences in the degree of occupation of the protruding orbitals and their hybridization as proposed by Knor and Müller (38).

Alternate bright and dim layers on the $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ planes are observed in case of ruthenium and not for rhenium (33). Melmed (34) proposed that the visibility, in the field-ion images, of alternate bright and dim layers decreases as the $c/a$ ratio increases. As the $c/a$ ratio increases, the field ripple over these two types of layers decreases, therefore making alternate layers more homogeneous for rhenium than for ruthenium. The $c/a$ ratio of titanium is closer to ruthenium than to rhenium; therefore alternate bright and dim layers on $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ planes are expected in case of titanium.

Another common feature observed for rhenium, ruthenium and cobalt is the alternate intensity of ledges around the (0001) planes. That is, on any one net plane of the (0001) type the intensity alternates with three fold symmetry around the plane. This has been attributed by Melmed (34) to the alternating ledge structure around the (0001) plane and by Müller (39) to the direction and type of electron orbitals.
Table 1. Comparison of Various Properties of Hexagonal Metals

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Metal</th>
<th>Z</th>
<th>(T(°K))</th>
<th>(c/a)</th>
<th>(H_F) (Kcal/mole)</th>
<th>(r(A))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rhenium</td>
<td>75</td>
<td>3453</td>
<td>1.6140</td>
<td>186</td>
<td>1.37</td>
</tr>
<tr>
<td>2.</td>
<td>Ruthenium</td>
<td>44</td>
<td>2700</td>
<td>1.5835</td>
<td>155</td>
<td>1.34</td>
</tr>
<tr>
<td>3.</td>
<td>Hafnium</td>
<td>72</td>
<td>2400</td>
<td>1.5870</td>
<td>146</td>
<td>1.59</td>
</tr>
<tr>
<td>4.</td>
<td>Titanium</td>
<td>22</td>
<td>1940</td>
<td>1.5873</td>
<td>113</td>
<td>1.47</td>
</tr>
</tbody>
</table>

In the Table
- \(Z\) = atomic number,
- \(T\) = melting point,
- \(H_F\) = heat of sublimation at 298° in Kcal/mole and
- \(r\) = atomic radius.
The order of pole prominence in the case of hexagonal metals (40) depends upon the R/c and c/a ratios, where R is the tip radius, c and a are hexagonal unit cell axis. In the computed images of HCP lattice, in general the order of pole prominence was as follows: \{0001\}, \{10\overline{1}0\}, \{10\overline{1}1\}, \{11\overline{2}0\} and \{10\overline{1}2\} poles. However, in these calculations of pole prominence, it was assumed that there is no influence of the environment on the surface and evaporation is uniform, leading to an equilibrium end form. In field-ion images of ruthenium and rhenium in helium (33, 34) the same order of pole prominence can be marked easily.
CHAPTER III

APPARATUS AND EXPERIMENTAL PROCEDURE

A. Materials

Marz grade titanium wire was used in these studies. A typical analysis of the bulk material from which the wire was prepared is given in Table 2.

The titanium had been zone refined by electron beam in vacuum of $10^{-6}$ torr. It was cold worked by swaging and drawing to wires of diameters 0.020 inch and 0.005 inch. The 0.020 inch diameter wire was vacuum annealed at 600°C for 30 minutes.

It is believed that the 0.005 inch diameter wire had picked up many impurities during cold working; therefore the 0.020 inch diameter wire was used in most of the experiments.

B. Specimen Preparation

The specimen preparation set up is shown in Figure 1. The titanium wire, approximately 0.5 inch long, was spot welded to a nickel loop. Tungsten loops were used for specimens to be heated in the microscope. A small amount of stop lacquer was put on the end of the specimen so that the lower end of the specimen was not etched during electropolishing and a fine neck was formed just above the lacquer-covered portion.

The electrolyte composition was as follows: 118 ml methanol, 70 ml n-butanol and 12 ml perchloric acid. The pH of this electrolyte
Table 2. Typical Analysis of MARZ Grade Titanium

<table>
<thead>
<tr>
<th>Impurity Element</th>
<th>Content (ppm)</th>
<th>Impurity Element</th>
<th>Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78</td>
<td>Mn</td>
<td>1.2</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>Mo</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>O</td>
<td>63</td>
<td>Nb</td>
<td>&lt; 6</td>
</tr>
<tr>
<td>N</td>
<td>6</td>
<td>Ni</td>
<td>5</td>
</tr>
<tr>
<td>Ag</td>
<td>0.1</td>
<td>Pb</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>Al</td>
<td>15</td>
<td>Pd</td>
<td>&lt; 0.15</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt; 0.02</td>
<td>Pt</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Ca</td>
<td>0.08</td>
<td>Rh</td>
<td>0.05</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.4</td>
<td>S</td>
<td>1.5</td>
</tr>
<tr>
<td>Co</td>
<td>0.4</td>
<td>Si</td>
<td>3.5</td>
</tr>
<tr>
<td>Cr</td>
<td>25</td>
<td>Sn</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>8</td>
<td>Ta</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>50</td>
<td>V</td>
<td>1.0</td>
</tr>
<tr>
<td>Hf</td>
<td>12</td>
<td>W</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>K</td>
<td>0.08</td>
<td>Zn</td>
<td>&lt; 0.25</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt; 15</td>
<td>Zr</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 1. Diagram Showing Specimen Preparation Set-Up
was 0.04 as measured by the pH meter. A stainless steel strip was used as the cathode. The beaker with the electrolyte was placed in a dry ice and acetone mixture.

The specimen was dipped in the solution briefly in order to cool it prior to applying the DC voltage. The etching occurred above the lacquer-covered portion of the wire. Initial etching was done at 60-65 volts. The voltage was then reduced to 30-40 volts when the neck became very fine. The lacquer was dissolved in acetone at this stage. Polishing was then continued until the lower part of the neck fell. The tip was checked for its sharpness by optical microscopy at a magnification of 400X. After preparing the specimen it was mounted in the microscope as soon as possible.

The sharpness and smoothness of the tip were greatly influenced by the polishing voltage and the temperature of the electrolyte. The tip was blunt and the shank was rough when the final polishing voltage was above 40 volts or when the electrolyte temperature was above -40°C.

C. Field-Ion Microscope

A bakeable all metal microscope was used in this study. A schematic diagram of the microscope is given in Figure 2. The microscope was equipped with a diffusion pump (D) backed by a mechanical pump (E) for achieving pressure in the $10^{-6}$ torr range. The microscope was also equipped with an ion pump and titanium sublimation pump (C) for achieving pressure in the range of $10^{-8}$ torr. The image gas was leaked into the system through a variable leak valve ($V_4$). Cylinders of research grade helium, neon and hydrogen were connected to the gas
A. Microscope Body
B. Fluorescent Screen
C. Ion Pump and TSP
D. Diffusion Pump
E. Mechanical Pump
F. Liquid N$_2$ Trap
G. Gas Cylinders
H. Liq. N$_2$ Trap
K. Pressure Manifold
L. Flexible Joint
M. Specimen Holder
V$_4$. Fine Leak Valve

Figure 2. Schematic Diagram of the Field-Ion Microscope
manifold for use as image gases.

The microscope head (A) was so designed that the specimen could be cooled to liquid nitrogen, hydrogen or helium temperatures. Liquid nitrogen could be poured directly into the specimen holder dewar (M) while liquid hydrogen was produced by inserting a cryo tip assembly into the dewar. Temperature close to that of liquid helium were obtained by transferring helium gas from a liquid helium reservoir to the specimen holder dewar. The specimen holding pins, which were located on the vacuum side of the specimen holder, were isolated from the rest of the assembly and were attached to a 25 KV dual feed-through. These high voltage leads were used for resistance heating the specimen and for applying the high positive potential to the tip. The high voltage DC supply ranged from 0-30 kilovolts. A fiber optics screen (B) was used for most of the work. A Varian nude ionization gauge was used to measure the pressure in the system.

D. Operation of the Field-Ion Microscope

The specimen was mounted on the two pins of the specimen holder and the high voltage wires were connected to the pins. The screen flange with a copper gasket was put on the microscope and the bolts were tightened to obtain a good vacuum seal.

Initial pumping of the microscope was done with the mechanical pump by opening valves \( V_1 \) and \( V_2 \) (Figure 2). The liquid nitrogen trap (F) had been filled to avoid any oil vapor back-streaming into the microscope. After 15-20 minutes, when the vacuum was less than \( 10^{-3} \) torr, \( V_2 \) was closed and \( V_5 \) was opened slowly. The titanium sublimation pump
was left on until the pressure was in the $10^{-6}$ range. Then the titanium sublimation pump was cut off, and system was left with the ion pump on until the pressure was in the $10^{-7}$ torr range. Meanwhile, the gas line was evacuated with the mechanical pump by opening valves $V_3$ and $V_6$.

When the microscope jacket and the specimen holder were filled with liquid nitrogen, the pressure of the system fell to approximately $10^{-8}$ torr. After the specimen had cooled for about 20 minutes, the gas line cold trap (H) was then filled with liquid nitrogen and $V_6$ was closed. The desired gas was admitted to the gas line by opening the appropriate valve ($V_7$, $V_8$ or $V_9$). Usually the gas line was filled to atmospheric pressure. The gas was leaked into the microscope body by slowly opening $V_4$. A continuous supply of gas at the desired pressure was maintained by adjusting $V_4$ and $V_2$. The voltage was then slowly applied to the tip. The image was viewed on a mirror placed below the fluorescent screen.

Most of the experiments on studying effects of gases were performed on tips cleaned by field evaporation in hydrogen at 78°C. The system was exposed to air by removing the flexible joint $V_3$ and then admitting the air to the desired pressure through this valve and $V_2$. Heating of the specimens was done in the microscope by applying 2-3 volts AC across the leads. The tungsten loops were used for these experiments. Usually the resistance of the tungsten loop was 0.5-1.0 ohm.

E. Metallography of Titanium Wire

The 0.020 inch diameter wire was cold mounted with ends outside the mount. These ends were used for electropolishing and anodizing
treatments. After mounting, the specimen was ground carefully using standard metallographic procedure on 240, 320, 400 and 600 grit silicon carbide papers. The specimen was washed thoroughly in water and then polished on 6 micron diamond paste on microcloth.

The specimen was electro-polished at -40°C with fresh electrolyte containing 118 ml methanol, 70 ml n-butanol and 12 ml perchloric acid. A stainless steel strip was used as the cathode. The electro-polishing was done for 6-8 minutes by applying 28 volts DC to the terminals after which the specimen was washed thoroughly and anodized.

The anodizing technique was the same as that developed at the Oak Ridge National Laboratories for zirconium and its alloys. The electrolyte contained 60 ml ethyl alcohol, 35 ml water, 20 ml glycerine, 5 ml phosphoric acid, 10 ml lactic acid and 2 grams citric acid. The stainless steel strip was used as the cathode. The anodizing was done by applying 20-24 volts DC for 5-10 secs after which the specimen was washed thoroughly in water and dried under an air dryer. The microstructure was studied by conventional techniques.
CHAPTER IV

RESULTS

A. Field-Ion Microscopy of Titanium

1. Hydrogen-Ion Microscopy

   a. Image Development. A series of micrographs showing the development of the titanium image in hydrogen ion microscopy is given in Figure 3. These micrographs were selected from a longer series in order to illustrate the several distinct stages that occurred during field evaporation and development of the titanium image.

   The pattern shown in Figure 3a appeared during the first stages of development of the image and presumably corresponded to a corrosion film on the specimen. As this outer layer was removed a second type of corrosion layer appeared in the image. This layer was characterized by intense random spots with no distinct image pattern. The intense spots near the center of the micrograph in Figure 3b represent the initial stages of development of the second corrosion layer. In this micrograph the first corrosion layer is still seen on the outer edges of the image.

   After further field evaporation, features of the titanium image became visible, as shown in Figure 3c. The \(\{10\bar{1}1\}\) regions of titanium were beginning to develop at this stage. Further field evaporation produced very dark \(\{10\bar{1}1\}\) regions and bright bands along zones passing through the \((0001)-(11\bar{2}0)\) planes and the \((10\bar{1}0)-(11\bar{2}0)\) planes. A micrograph at this stage is shown in Figure 3d. Micrographs taken after
(a). Image at 11.5 KV of Initial Outer Layer

(b). Image at 13.2 KV Showing Oxygen Rich Layer Developing in the Center. The First Layer is Still Seen on the Outer Edges

Figure 3. Series of Micrographs Showing the Image Development in Hydrogen-Ion Microscopy at 78°K

(Continued to next page)
Figure 3. (Continued) Series of Micrographs Showing the Image Development in Hydrogen-Ion Microscopy at 78°K
(Continued to next page)
(e). Image at 17.0 KV Showing Platelets Lying on a Plane in the Zone Passing Through (0001)-(1120) Planes

Figure 3. (Continued) Series of Micrographs Showing the Image Development in Hydrogen-Ion Microscopy at 78°K
further field evaporation revealed thin platelets as shown in Figure 3e. The traces of these platelets were lying perpendicular to the zone passing through the (0001)-(1120) planes.

Each platelet disappeared after evaporation of 10-12 layers of (1120) planes, which corresponded to a 15-18 Å depth of platelet going into the matrix. During the process of field evaporation platelets were constantly being removed and new ones were appearing at different positions. Approximately 8-12 platelets were found on each micrograph.

The micrographs in Figure 3 were taken on a 35 mm camera. Micrographs taken on the fibre optics screen revealed the platelets and other features of the titanium image more clearly as shown in Figure 4.

b. Image of a Grain Boundary. In one specimen a grain boundary was observed as shown in Figure 5. Some segregation along the grain boundary can be seen in the micrograph. The specimen flashed before it could be developed sufficiently to index the pattern.

c. Effect of Hydrogen Pressure on Evaporation Voltage. In this experiment the change in voltage required for a constant evaporation rate was measured as a function of hydrogen pressure. The hydrogen-ion image of titanium was unstable at 78°K, therefore the voltage to evaporate 10 layers of (1120) planes per minute was measured at hydrogen pressures ranging from $1 \times 10^{-4}$ to $8 \times 10^{-4}$ torr. The results are given in Table 3. A graph showing the effect of hydrogen pressure on evaporation voltage is plotted in Figure 6. After the pressure exceeded $6 \times 10^{-4}$ torr there was no further decrease in voltage required to evaporate 10 layers of (1120) planes per minute.

These results indicate that at lower hydrogen pressure the
(a). Hydrogen-ion image at 13.0 KV taken on fiber optics screen

(b). Stereogram corresponding to (a)

Figure 4. End Form of Titanium in Hydrogen-Ion Microscopy
Figure 5. Hydrogen-Ion Image at 11.0 KV Showing Hydrogen Segregation at a Grain Boundary in Titanium
Table 3. Data on Hydrogen Pressure Versus Evaporation Voltage

<table>
<thead>
<tr>
<th>Hydrogen Pressure (torr)</th>
<th>Voltage Required to Evaporate 10 Layers/Minute of (1120) Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>8.7</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>8.4</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>8.2</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>8.15</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>8.10</td>
</tr>
<tr>
<td>$6 \times 10^{-4}$</td>
<td>8.08</td>
</tr>
<tr>
<td>$7 \times 10^{-4}$</td>
<td>8.08</td>
</tr>
<tr>
<td>$8 \times 10^{-4}$</td>
<td>8.08</td>
</tr>
</tbody>
</table>
Figure 6. Curve for Field Evaporation Voltage Versus Hydrogen Pressure
evaporation was controlled by the supply of hydrogen. As the hydrogen pressure was increased, the evaporation voltage decreased due to a greater supply of hydrogen and subsequent interaction. At the pressure of $6 \times 10^{-4}$ torr the supply of hydrogen was no longer the rate controlling factor and then the evaporation rate was controlled by the activation energy required for titanium to evaporate. The evaporation rate did not change as the hydrogen pressure was increased further.

**d. Images From 0.005 Inch Diameter Wire.** Smaller diameter wire was used to study the effect of impurities on image characteristics of titanium. Several field-ion microscope specimens were prepared from this wire. The hydrogen-ion images from these specimens showed only random spots. These spots increased in number and filled the whole screen as the voltage was raised. The image showed only random spots even after raising the voltage by 15 KV. Platelets were not observed in these images. The regular titanium image could not be obtained from this wire because of high impurity content, presumably oxygen picked up during cold working to such a fine diameter. It is therefore difficult to get good field-ion images from very fine wires.

2. **Neon-Ion Microscopy**

Some form of image intensification is necessary for neon-ion microscopy, therefore these experiments were performed by the author at the University of Florida with their micro-channel plate converter. The background pressure in this system was generally $1 \times 10^{-7}$ torr and a static image gas supply was used.

Several specimens were observed in neon-ion microscopy at $21^\circ$K. Initially a few random spots appeared on the image. The best image that
was developed revealed a few net planes edges of the \{10\overline{1}1\} type, but
the rest of the image consisted of random spots as shown in Figure 7.

The odd donut shaped spots in the micrograph are believed to be
due to residual gases in the microscope. These donut shaped spots were
fewer in number immediately after changing the image gas but became pro­
gressively more dense as time elapsed after changing the gas.

3. Helium-Ion Microscopy

a. Without Micro-Channel Plate. Most of the efforts to image
titanium in helium-ion microscopy were performed without the use of a
microchannel plate. At liquid nitrogen temperature the specimens flashed
in all cases before an image could be obtained. When the specimen was
cooled to lower temperatures with cold helium gas, the cross pattern,
which is characteristic of the initial titanium image as described in
section A-1-a did appear before the specimen fractured.

b. With Micro-Channel Plate. One of the specimens which had
been imaged in neon as previously described in section A-2, was then
imaged in helium at 21°K. The initial pattern in helium consisted of
spots in a cross pattern passing through (0001)-(11\overline{2}0) planes. The
regions around \{10\overline{1}1\} planes appeared dark. Later the \{10\overline{1}0\} and (11\overline{2}0)
regions became well developed and a few spots appeared in the \{10\overline{1}1\}
regions as shown in Figure 8a. After further field evaporation the
\{10\overline{1}1\} regions began to develop and several net plane edges were visible
as shown in Figure 8b. The field was above the best image voltage so
that the evaporation was occurring during photographing. Therefore, the
fine details of the image were not resolved in these photographs. The
alternate bright and dim rings were barely discernible on \{10\overline{1}0\} planes.
(a). Neon-ion image of titanium at 21°K showing random spots and a few net plane edges in the \{10\overline{1}\} regions

(b). Stereogram corresponding to (a)

Figure 7. Neon-Ion Microscopy of Titanium at 21°K
(a). Image at 11.8 KV Showing Bright Bands and Very Few Spots on the \{10\overline{1}1\} Regions

(b). Image at 13.5 KV Showing Further Development of the \{10\overline{1}1\} Regions

**Figure 8.** Development of Titanium Image in Helium-Ion Microscopy at 21°K

(Continued to next page)
Figure 8. (Continued) Development of Titanium Image in Helium-Ion Microscopy at 21\textdegree K.
but not on \{10\overline{1}1\} and (11\overline{2}0) planes. The specimen flashed before the image could be fully developed. The platelets which were found during hydrogen-ion microscopy were not observed in the helium-ion images.

Some large random bright spots can be seen in Figure 8a. The number of large bright spots decreased as the voltage was raised. These large spots were probably due to impurity-gas interaction within the microscope. Changing the image gas decreased the number of these spots initially, but after a few minutes they reappeared and increased in number with time.

B. Reaction of Gases With Titanium

The following experiments were performed with titanium specimens which had been field evaporated and imaged in hydrogen. A clean tip refers to one from which the corrosion layers had been removed as described in section A-1-a so that the bare titanium metal was exposed.

1. Hydrogen at 78°K

After obtaining the clean tip the field was cut off and hydrogen at a pressure of 2.5 \times 10^{-4} torr was kept flowing through the system for five minutes. Then the specimen was re-imaged in hydrogen. When the voltage, at which the field had been cut off, was reached many extra spots showed in the image. It was necessary to raise the voltage by an additional 0.33 KV in order to get an image of the same quality as that prior to cutting off the field.

The experiment described above was performed also with hydrogen exposure time of 10 and 20 minutes (with field off). Each time an additional 0.33 KV was required to reproduce an image of the same quality as that before cutting off the voltage. This extra 0.33 KV is due to any
interaction of hydrogen at 78°K as well as the field promoted gas etching effect when the voltage was being applied.

2. Hydrogen at Elevated Temperature

The following experiment was performed in an effort to increase the hydrogen concentration in titanium and to observe changes, if any, in the number and size of platelets.

A clean titanium tip was obtained as shown in the micrograph in Figure 9a. The voltage was cut off and hydrogen was left flowing through the system at pressure of $1 \times 10^{-4}$ torr. The specimen was resistance heated for 15 minutes at approximately 200°C. Liquid nitrogen was left in the specimen holder so that the specimen cooled very quickly to 78°K when resistance heating was discontinued.

The voltage was applied to re-image the specimen. At the same voltage where the specimen had contained many platelets, only a few platelets were found as shown in the micrograph in Figure 9b. The regions around the $\{10\overline{1}1\}$ planes appeared darker than in the previous image at this voltage. It was necessary to raise the voltage an additional 1.5 KV to get the same density of platelets as in Figure 9a.

3. Residual Gases at Room Temperature

Frequently specimens which had been observed in hydrogen-ion microscopy were left over-night in the microscope so that the experiments could be continued the next day.

When the specimens were re-imaged in hydrogen, random spots mainly along the cross bands appeared initially. As the voltage was raised, the number of bright spots increased and facets of $\{10\overline{1}1\}$ planes appeared. At the voltage, where the experiment had been discontinued the previous
(a). Image Showing Platelets Before Heating

(b). Image After Heating Showing Fewer Platelets and Darker \( \{10\overline{1}1\} \) Regions

Figure 9. Hydrogen-Ion Images of Titanium at 78°K and 9.0 KV Before and After Heating in Hydrogen
day, the image quality was not good. As the voltage was raised by an additional 0.3 to 0.4 KV, an image of the same quality as that of the previous day was achieved.

This loss in voltage of 0.3 to 0.4 KV was probably due to the interaction of residual gases at room temperature as well as hydrogen etching during the period when the voltage was being applied.

4. Residual Gases at Elevated Temperature

A clean titanium tip was obtained at 11.5 KV; the voltage was then lowered, hydrogen was evacuated and the system was warmed to room temperature. The next day, when the system pressure was $4.2 \times 10^{-8}$ torr, the specimen was resistance heated for 20 minutes at approximately 240-300°C. The background pressure during heating was approximately $1 \times 10^{-7}$ torr.

The specimen was then cooled to 78°C and then imaged in hydrogen. A series of micrographs showing the image development in hydrogen is given in Figure 10. The development of the image was quite similar to that of specimen described in section A-1-a.

Initially random spots were observed mainly along the cross bands with maximum brightness in the center as shown in Figure 10a. As the surface layers evaporated the inner oxygen rich layer became visible. Figures 10b-10d show that the outer surface layer is being removed and the inner layer is becoming more prominent.

After evaporation of these corrosion layers, the features of titanium became visible. In Figure 10e the titanium $\{10\bar{1}1\}$ regions are shown developing and the first corrosion layer is at the sides forming a ring shape. As the voltage was raised further the titanium image developed with recessed $\{10\bar{1}1\}$ regions and with platelets parallel to
Figure 10. Micrographs Showing Image Development in Hydrogen at 78°K After Heating in Vacuum

(Continued to next page)
(c). Image at 9.9 KV Showing Development of Inner Oxygen Rich Layer

(d). Image at 10.25 KV Showing Further Development of the Inner Layer

Figure 10. (Continued) Micrographs Showing Image Development in Hydrogen at 78°K After Heating in Vacuum

(Continued to next page)
(e). Image at 11.0 KV Showing Initial Development of \{10\overline{1}\} Regions of Titanium. The Outer Corrosion Layer Appears as a Ring at the Sides of the Specimen

(f). Image at 12.0 KV Showing Platelets and \{10\overline{1}\} Facets

Figure 10. (Continued) Micrographs Showing Image Development in Hydrogen at 78°K After Heating in Vacuum
a plane in the zone passing through (0001)-(1120) planes, as shown in Figure 10f.

5. Air at Elevated Temperature

In this experiment a clean titanium tip was obtained at 10.2 KV; the voltage was then lowered and the hydrogen evacuated. The microscope was warmed up to room temperature with a background pressure of \(2.5 \times 10^{-8}\) torr. Air was leaked into the system at a pressure of \(2.5 \times 10^{-4}\) torr.

The tip was then heated to approximately 250-300°C for five minutes. During this time the pressure in the system decreased to \(1 \times 10^{-4}\) torr. Thereafter the system was left pumping for a few hours to obtain a good vacuum, after which the specimen was again imaged in hydrogen at 78°C.

Random spots appeared at 8.5 KV and as evaporation continued the number of bright spots increased until screen was full at 10.0 KV. The specimen was field evaporated at 11.5 KV and then imaged at 10 KV. The micrograph taken at this voltage which revealed many small oxide grains, is shown in Figure 11a.

When the field was raised well above that for the best image, the resolution became poor; but at the same time the grain boundaries of surface oxide film became much more prominent in the image as shown in the micrograph in Figure 11b. A sketch of the grain boundaries is given in Figure 11c.

C. Metallography of Titanium Wire

The microstructure of titanium wire is shown in the optical micrograph in Figure 12. Equiaxed polyhedral grains of titanium were seen under the microscope. A large number of fine twins are also seen in the
(a). Image at 10.0 KV of Many Small Oxide Grains

(b). Image at 12.0 KV Showing Grain Boundaries of the Surface Oxide Film

Figure 11. Hydrogen-Ion Images at 78°K of Surface Oxide on Titanium Formed by Heating in Air

(Continued to next page)
(c). Sketch of grains in (a) and (b).

Figure 11. (Continued) Hydrogen-Ion Images at 78°K of Surface Oxide on Titanium Formed by Heating in Air.
Figure 12. Micrograph of Titanium Wire - 500 X
micrograph. These twins are presumably annealing twins. Twinned grains, when observed with the optical microscope, develop contrast on different sides of the twinning plane. This type of contrast was confirmed in this case by slightly rotating the specimen on the stage of the microscope thereby indicating that there were no hydrides or second phase particles in the titanium matrix.
CHAPTER V

DISCUSSION OF RESULTS

A. Field-Ion Microscopy of Titanium

In all attempts to image titanium with helium at liquid nitrogen temperature, without microchannel plate converter, the specimen flashed before an image could be obtained. Images in helium at cold helium gas temperature, without the microchannel plate converter, only revealed the cross pattern, which is characteristic of the initial titanium image. The specimen fractured before the image could be further developed.

The good quality images in helium were obtained at 21°K using a microchannel plate converter. The advantage of using microchannel plate converter are two-fold. First, the lower gas pressure in the range of $10^{-5}$ torr reduces the amount of gas impurities. Second, the chances of flashing the specimen are reduced because the image can be seen on the screen even when the ionization and field evaporation rates are very low; thus the field evaporation rate can be controlled during the initial evaporation. This is when the rate of applying potential is most critical to prevent flashing.

The gain in image quality at lower temperatures is attributed to two factors: a) the ratio of the evaporation field to the best image field is higher at 21°K than at 78°K and b) reduced contamination problem due to cryogenic pump (21°K), which traps most of the residual gases. The corrosion problem is reduced because residual gases like hydrogen, oxygen, water vapor and nitrogen are ionized at a lower potential than
to helium in helium-ion microscopy. However, gases adsorbed on the speci-
men shank may migrate to low field regions of the specimen and present a 
corrosion problem. This problem is especially critical in imaging a 
highly reactive material like titanium. Since a static gas supply was 
used in the microscope with the microchannel plate converter, the impurity 
gas content built up during imaging. It was necessary to change the 
image gas supply frequently, which was not the case for other metals 
imaged in this microscope. Imaging in a static gas supply may not cause 
deterioration of field-ion images of other metals, but for titanium a 
dynamic gas supply is needed to prevent this. In neon-ion microscopy 
was even more susceptible to gas impurities because of the lower field 
for neon ionization. Therefore, the neon-ion images of titanium showed 
only random spots with a few net plane edges on the \([10\overline{1}]\) planes.

The hydrogen-ion images at 78°K do not reveal the atomic structure 
of the surface, but the surface topography is clearly projected. Since 
hydrogen interaction produces large variation in the radii of curvature 
on the specimen surface, it is difficult to image the entire surface at 
best image potential. Furthermore, the evaporation field and the best 
image potential are not separated at 78°K, due to the field promoted 
etching in hydrogen; therefore during imaging some evaporation always 
continues and the hydrogen-ion images of titanium at 78°K are unstable.

B. Surface Films

Surface films were found on all titanium field-ion specimens 
initially, as described in section IV-A-1. Similar surface films were 
found on specimens heated in residual gases in the microscope, as de-
scribed in section IV-B-4. The observed films can be explained by the
oxidation of titanium.

The oxygen interaction with the titanium surface causes a solution of oxygen in titanium until the oxygen content is high enough to form an oxide on the surface. Therefore, as the oxide film on the titanium surface was removed by field evaporation, the inner oxygen rich layer was exposed. The possible causes for surface films on electrolytically prepared specimens are (1) oxidation during electrolytic etching of the specimen and (2) oxidation in air exposure of the titanium tip after preparation. Oxidation of specimens heated in residual gases resulted from the reaction with water vapor in the microscope or dissolution of oxide on the shank of the specimen which was not cleaned by field evaporation.

Images from the above surface films did not show any net plane rings, as observed for oxide formed on specimens heated in air, as described in section IV-B-5. This may be the result of two factors:

(1) The oxidation of titanium during electro-polishing and during heating at low pressures may have been so slow that the supersaturation was not high enough to produce the regular oxide, TiO₂.

(2) The surface film may have been too thin to develop a regular image during field evaporation.

An additional observation in favor of factor (1) was the single crystal appearance of surface films formed electrolytically or by low pressure heating compared to the small grain size of the oxide formed by heating in air. The nucleation rate in the latter specimens was apparently quite high due to the higher oxygen pressure and larger supersaturation.
C. Surface Energy of Titanium in Hydrogen Environments

In hydrogen-ion images of titanium the \(\{10\bar{1}1\}\) regions appeared dark, as described in section IV-A-1. Initially, images in helium-ion microscopy also appeared dark around the \(\{10\bar{1}1\}\) regions, as described in section IV-A-3. During field evaporation in helium, however, these regions began to develop, so that the final end form in helium would probably be similar to that for other HCP metals. From these observations it is proposed that preferential etching or faceting of the \(\{10\bar{1}1\}\) titanium planes occurs in hydrogen. Figure 13 schematically shows the profile of a tip with \(\{10\bar{1}1\}\) facets. In hydrogen the interplanar binding energy of the \(\{10\bar{1}1\}\) planes is lowered more than that of other planes; hence these planes evaporate more readily than other regions and therefore develop more prominent facets in hydrogen than in helium-ion microscopy.

The lowering of the interplanar binding energy can be expressed as the lowering of the surface free energy. The change in the surface free energy in the presence of adsorbed gases is given by the equation given below (41):

\[
\left(\frac{\partial \gamma}{\partial \mu_i}\right)_T = -\kappa_i
\]

for \(i\) th component

where \(\gamma\) = surface free energy
\(\mu_i\) = chemical potential of the \(i\) th component and
\(\kappa_i\) = surface excess of the \(i\) th component or number solute atoms absorbed per unit area.

From this equation it is seen that the change in surface free energy depends not only on amount of hydrogen adsorbed, but also on the
(a) Sketch showing the dark \{01\bar{1}1\} areas in Figure 8b

(b) Sideview sketch of the field-ion specimen showing facets of \{10\bar{1}1\} regions

Figure 13. \{10\bar{1}1\} Facets of Titanium in FIM Images
partial molar free energy change due to adsorption. Since hydrogen is present over all of the surface during imaging and evaporation, it is proposed that the surface energy of the \{10\overline{1}1\} planes is lowered to a greater extent than that of other planes primarily due to the specific hydrogen interaction on these planes.

An additional observation in support of the above interpretation is the following: when a titanium specimen was heated in hydrogen, as described in section IV-B-2, the \{10\overline{1}1\} facets were even more prominent than those formed during field evaporation in hydrogen. These results confirm the lowering of the surface energy of titanium \{10\overline{1}1\} planes in the presence of hydrogen.

It is reported in this work that the surface energy of the \{10\overline{1}1\} planes is lowered more than that of \{10\overline{1}0\} planes. This may be due to the different interaction of hydrogen with these planes. A second possibility, however, is oxygen strengthening of the \{10\overline{1}0\} planes. Interstitial oxygen increases the binding energy or melting point of titanium, as shown in Figure 14.

Interstitial oxygen in titanium occupies octahedral positions between \{0001\} planes. A hexagonal unit cell with interstitial oxygen is shown in Figure 15. In Figure 16 the \{10\overline{1}0\} and \{10\overline{1}1\} planes are shown with interstitial oxygen at octahedral sites. The ratio of oxygen atoms in the \{10\overline{1}0\} plane to those in the \{10\overline{1}1\} plane is 5:3 when all the interstitial sites are filled. Therefore, strengthening of \{10\overline{1}0\} planes may be more than that of \{10\overline{1}1\} planes, because of the higher oxygen concentration.

However, the relative strengthening due to oxygen atoms may not
Figure 14. Partial Titanium - Oxygen Phase Diagram.
Figure 15. Hexagonal Unit Cell With all the Octa-hedral Sites Occupied by Oxygen Atoms.
No. of oxygen atoms in area 2ac on (10\overline{1}0) = 5
No. of oxygen atoms in area 2ac on (10\overline{1}1) = 3

Figure 16. Projection of Planes of HCP Cell With Oxygen at Octa-hedral Sites.
be very pronounced because no \{10\overline{1}1\} facets were seen in the oxygen rich layers on titanium surface during hydrogen imaging. Moreover, the images from 0.005 inch diameter wire with probable higher oxygen content did not show any facets. Therefore, it is concluded that the surface energy of the \{10\overline{1}1\} planes is lowered to a greater extent due to the specific interaction of hydrogen with these planes.

**D. Hydrogen Segregation in Titanium**

After removal of surface layers all specimens imaged in hydrogen showed thin platelets, as described in section IV-A-1. These platelets are believed to be either hydride or hydrogen segregation at defect sites.

Since helium-ion images of titanium did not show any platelets, it is assumed that the original wire and the electro-polished specimens did not contain such platelets. The hydrogen interaction at 78°K in the presence of a high field seems to be the cause for these platelets. The appearance of these platelets may be explained as follows: The high voltage on the tip causes large outward stresses on the specimen surface which increases the interplaner spacings. The widely spaced \{0001\} planes assume metastable positions with larger interplaner spacing. This effect is concentrated at the higher field apex region. Hydrogen absorption and diffusion along these planes is enhanced. Microsegregation of hydrogen at lattice defects such as dislocations, vacancies, stacking faults and twinning planes would then produce a platelet like appearance. In one of the specimens segregation along a grain boundary was also observed, as described in section IV-A-1.

The brightness of these platelets can be the hydrogen atom taking
over a small fraction of electronic charge of the adjacent titanium atom. The polarization of the protruding atom is thus increased to produce a higher local field and thereby enhance ionization. A similar explanation has been used to explain increased brightness of hydrogen promoted helium images of metals (30).

Further work, however, is required to confirm whether these platelets are due to thin hydrides or hydrogen segregation. These platelets were parallel to a plane in the zone passing through the \( \{0001\} \) -\( \{11\overline{2}0\} \) planes, most probably the \( \{0001\} \) plane. Therefore, if they do represent thin hydrides or hydrogen segregation, they are on a different plane from the proposed \( \{10\overline{1}0\} \) (12).
CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The field-ion microscopy of titanium and interactions of titanium with hydrogen, residual gases and air have been studied. The following conclusions are drawn:

1. High purity annealed titanium specimens, prepared very carefully at -40°C with final polishing voltage lying between 30-40 volts, can give rise to good titanium images in field-ion microscopy.

2. Surface films are formed on electropolished titanium specimens. These surface films appeared to be different from those formed by oxidation in air at elevated temperatures in the following ways: the surface films resulting from electropolishing showed a much higher degree of epitaxy and probably were not the normal TiO2 oxide.

3. Stable titanium images can be obtained by using low gas pressure (with microchannel plate converter) of helium at 21°K.

4. Field evaporated end forms of titanium in helium are more hemispherical than in hydrogen-ion microscopy.

5. Hydrogen-ion images of titanium at 78°K develop facets around the {1011} planes. These facets are attributed to the preferential lowering of the surface energy of these planes in hydrogen.

6. Platelets were observed in hydrogen-ion images and were found to be lying parallel to a plane in the zone passing through the (0001)-
(1120) planes. These platelets may represent thin hydrides or hydrogen segregation at defect sites, formed by the interaction of titanium with hydrogen during hydrogen-ion microscopy.

B. Recommendations

In the present studies good quality helium-ion images of titanium have been obtained and research can be done to understand the gas interactions at an atomic level. The specific interaction of hydrogen with titanium \( (10\overline{1}1) \) planes has been interpreted as lowering of surface energy of these planes due to hydrogen interaction. Also thin platelets have been observed in hydrogen-ion images of titanium. These platelets along with the effect on surface energy due to hydrogen interaction may play an important role in SCC of titanium and its alloys. For better understanding of these aspects research needs to be extended to other transition metals and titanium base alloys. The following is a partial list of recommended research, which could lead to better understanding of hydrogen-metal interactions.

1. To study the surface energy changes of titanium alloys which fail under stress-corrosion environments. This could be done by hydrogen-ion microscopy and thermal faceting experiments.

2. To study surface effects of hydrogen on other transition metals like iron, nickel, copper, etc.

3. To study the hydrogen segregation or thin hydride platelets by use of helium-ion microscopy, after hydrogenating the samples.

4. To study field-ion images of titanium with higher hydrogen content in the matrix and thus correlate the effect of absorbed hydrogen
on surface energy changes.

5. To study the nature, distribution and size of hydride precipitates in titanium specimens treated at elevated temperature under high hydrogen pressure.
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