AN INVESTIGATION OF THE EFFECT OF SURFACE IMPURITIES ON THE ADSORPTION KINETICS OF HYDROGEN CHEMISORBED ONTO IRON

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1.0 INTRODUCTION

The original goal of this program was to investigate the effect surface impurities have on the heterogeneous kinetic processes of those molecular species which produce gaseous hydrogen degradation of the mechanical properties of metallic structural materials. However, shortly after the initiation of the original program, the program's NASA Technical Monitor, Dr. Howard Nelson, requested that the effort supported by this Co-operative Agreement be redirected to study more pressing materials issues associated to the development of the National Aero-Space Plane (NASP). The results of these efforts are outlined in this report. Detailed discussions of specific work, including experimental techniques and procedures, will be found in the publications listed with the subsection discussing that specific work as well and in Section 5. No inventions were generated or disclosed within this Agreement.

1.1 Impurity Related Study

Although hydrogen degradation of metallic materials is believed to result from dissolved protonic hydrogen [1], the heterogeneous hydrogen interface transport processes often dominate the kinetics of degradation [2]. The initial step in the interface transport process is the dissociative chemisorption of the molecular species at the metal surface followed by hydrogen absorption into and transport through the bulk [3]. Steel is an important structural material that is subject to hydrogen embrittlement [1]. To evaluate the influence of the chemisorption process on the embrittlement kinetics for steel, the chemisorption of molecular hydrogen, $H_2$, and hydrogen sulfide, $H_2S$, on pure iron surfaces was investigated in an earlier study [4]. This work demonstrated that these gaseous molecules chemisorb via an adsorbed molecular state. This adsorbed molecular state can act as a rate-limiting step for the chemisorption process depending upon the gas phase pressure and surface temperature.

The surface of structural steel in service is more complicated than a pure iron surface. It can be covered by impurities introduced by the environment as well as alloying additions which have diffused to the surface from the bulk. The specific goal of the original study initiated under this Agreement was to characterize the changes produced in the $H_2$ and $H_2S$ chemisorption kinetics by typical steel grain boundary impurities, such as oxygen, sulfur, phosphorous, and arsenic. The change in the direction of the program in 1987 limited this study to just the effects of oxygen. The kinetics and the chemisorption process were monitored using the Chemisorption-Induced Resistance Change (CIRC) for adsorption onto thin polycrystalline iron film substrates and Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) for adsorption onto oriented iron film substrates.

1.2 NASP Hydrogen-Materials Study

Modern advanced aerospace applications require the use of structural materials in high pressure hydrogen environments at temperatures which range from low cryogenic temperatures to very high temperatures (1300 K and greater) [5]. Materials proposed for these applications, such as the titanium aluminides, beta-titanium alloys, iron-, nickel- and cobalt-based superalloys, and molybdenum-rhenium alloys need to possess a high degree of immunity from hydrogen induced degradation of mechanical properties. Initially, little was known about the interaction of hydrogen with many of these materials and the possible influence of hydrogen on the material's mechanical properties [6]. It was expected that the interaction of gaseous environmental hydrogen with these materials would be influenced by the gas phase-surface reaction process as well as the bulk transport...
process [7]. A revised agenda was established in 1987 to develop an understanding of the interaction of gaseous hydrogen with these materials and to evaluate hydrogen transport through them. Most of these studies, especially the surface studies, were of a "scoping" nature and are therefore not complete. Hydrogen surface reactions were studied using Auger electron spectroscopy, reflected electron loss spectroscopy, and work function changes. Bulk hydrogen transport was investigated with classical gas phase hydrogen permeation techniques [8].

2.0 SURFACE RELATED INVESTIGATIONS

2.1 Simple Adsorption

The goal in the majority of the fundamental studies that follow was to characterize and understand the nature of the basic chemisorption process and determine the kinetic rates for the indicated systems. Secondary was the accumulation of data on the origin of the chemisorption-induced resistance change. The more applied work performed for the NASP Hydrogen-Materials Compatibility program was directed toward ways to detect the presence of hydrogen on the surface and finding ways to mitigate its influence on material properties.

2.11 H₂:Fe

Under a previous grant, NASA NSG-2222, an extensive experimental study was made of the isothermal kinetics for hydrogen chemisorption onto polycrystalline evaporated thin iron films. These measurements were made over a temperature range from about 295 to 460 K and for hydrogen pressures up to about 10⁻² N/m² (8x10⁻⁵ Torr). The chemisorption kinetics were measured by using the chemisorption-induced resistance change to monitor the coverage of the chemisorbed hydrogen as it responded to changes in the gas phase pressure.

Under the present agreement (NASA NCC-2-63) the data from the earlier measurements (adsorption kinetics, desorption kinetics, pressure-jump relaxation kinetics, and equilibrium isotherms) were analyzed in terms of a simple chemical reaction kinetic model. The results of the completed study demonstrate that dissociative hydrogen chemisorption onto iron films occurs via an adsorbed molecular state (precursor). Desorption from the chemisorbed state to the gas phase is rate limited by desorption from the adsorbed molecular state to the gas phase for temperatures above 260 K. Adsorption from the gas phase to the chemisorbed state can also be rate limited by the adsorbed molecular state depending upon the temperature and gas pressure, a result with implications for the rate of hydrogen embrittlement in iron-based alloys. The absolute rate constants of the model obtained from the analysis were found to be independent of coverage for estimated coverage’s less than 0.8 monolayer. The pre-exponential factors for the rate constants are in good agreement with estimates from absolute rate theory.

This work demonstrated that the chemisorption-induced resistance change is a useful tool for investigating isothermal chemisorption kinetics. The technique is especially applicable to hydrogen chemisorption and does not interfere or modify the chemisorption process.

Published articles relevant to the H₂:Fe studies are listed in Section 5 as follows: 5,13,14,22,23 with presentations listed in Section 6 as follows: 1,5,36,37,51,52.
H$_2$:Be

This was a very limited study to determine the extent that gaseous hydrogen might adsorb onto the surface of clean beryllium. The adsorption of hydrogen onto beryllium was studied with Auger electron spectroscopy, reflected electron loss spectroscopy, thermal programmed desorption, and surface potential measurements. The ion-sputter cleaned beryllium surface at temperatures of 150, 290, and 800 K was exposed to hydrogen pressures up to $3 \times 10^{-3}$ N/m$^2$ ($2.3 \times 10^{-5}$ Torr).

The only evidence of molecular hydrogen adsorption onto clean beryllium was obtained with the surface potential measurement. The sticking coefficient at 290 K was estimated to be $4 \times 10^{-3}$ for molecular hydrogen with a very small change in the surface potential, implying a very small hydrogen surface coverage. The clean surface was characterized with the available electron spectroscopes. The published article relating the results of the H$_2$:Be study is listing 43 in Section 5 with the presentation listed in Section 6 at 29. This work was undertaken as part of the NASP Hydrogen-Materials Compatibility Program.

2.13 H$_2$:Titanium Aluminide Alloys

Surface manifestations of the interaction of hydrogen with a series of titanium-aluminum intermetallic alloys were investigated in this study. The alloys, which contained ternary additions, had nominal compositions of Ti$_3$Al, TiAl, and TiAl$_3$.

The surface hydrogen was derived from two sources; (1) dissociative adsorption of H$_2$ at low pressure ($6.6 \times 10^{-3}$ N/m$^2$, $5 \times 10^{-3}$ Torr) onto the clean alloy surface at ambient temperature (295 K), and (2) hydrogen dissolved into the bulk by pre-charging in a high temperature (873K), high pressure ($10^5$ N/m$^2$) hydrogen environment. Pre-charging can produce bulk hydride phases in these alloys, especially the Ti$_3$Al alloys. Auger electron spectroscopy and reflected electron energy loss spectroscopy were the techniques employed in the study.

Hydrogen induced changes in the titanium Auger spectra for the alloys were either very small or not observed in this work. This is in contrast to similar studies with pure titanium, where changes to the titanium Auger spectra are easily observed, especially when the hydride phase is present. Changes were observed, however, in the Auger spectra of some of the alloying elements. Shifts in the plasmon loss energy to higher energy were observed. Although the magnitude of the shifts depended upon the alloy composition, the shifts produced by adsorbed hydrogen on the clean surface agreed with the shift obtained with preadsorbed hydrogen.

Published articles relevant to the H$_2$:Titanium Aluminide studies are listed in Section 5 as follows: 17,19,29,26 with presentations listed in Section 6 as follows: 15,18,19,25,30,32,39,40. This work was undertaken as part of the NASP Hydrogen-Materials Compatibility Program.

2.14 H$_2$S:Fe

Work to understand the chemisorption kinetics of H$_2$S onto evaporated iron films was initiated under an earlier grant, NASA NSG-2222 and completed under the present agreement, NASA NCC-2-63. A gaseous environment containing H$_2$S is known to be significantly more aggressive in embrittling iron alloys than gaseous H$_2$ alone. Since it has been determined that the H$_2$ dissociative chemisorption rate is limited under typical service conditions (see section 2.11), a faster or more rapid adsorption rate (i.e., the chemisorption step is not rate limited) by the H$_2$S molecule may explain the enhanced embrittlement rate observed with H$_2$S. Use of H$_2$S is also a standard procedure for doping a sulfur onto a clean surface.
The kinetics of H$_2$S adsorption onto epitaxially grown [111] oriented iron films was measured using Auger electron spectroscopy and low energy electron diffraction at about 295 K. The adsorption data was interpreted by a model which assumed that dissociative chemisorption occurred via an adsorbed molecular state. The absolute rate constants for the model were estimated and utilized to interpret the kinetics for H$_2$S adsorption onto polycrystalline, evaporated, thin iron films, where the adsorption process was monitored with Auger electron spectroscopy as well as the chemisorption-induced resistance change. This work demonstrated that the kinetics for H$_2$S adsorption onto iron was essentially equal to that for H$_2$ adsorption onto iron under similar conditions.

Published articles relevant to the H$_2$S:Fe studies are listed in Section 5 as follows: 2,10,13 with presentations listed in Section 6 as follows: 1,2,3,8,27,36,37,46,48.

2.15 O$_2$:Fe

An extensive series of measurements was undertaken to study the adsorption of oxygen on evaporated, thin polycrystalline iron films. In this work, the film thickness was varied from 0.2 nm to 200 nm and film temperature during adsorption was varied from 220 to 450 K. There were three objectives in this work. The first was to calibrate the chemisorption-induced resistance change with the coverage of oxygen on the surface, an important first step in the impurity studies that followed. The second was to investigate further the origin of the resistance change, and the third objective was to investigate the chemisorption kinetics for this system. The majority of the work utilized the chemisorption-induced resistance change with a few measurements employing Auger electron spectroscopy.

Since the fractional chemisorption-induced resistance change, $\delta R/R$, is inversely proportional to the film thickness, $d$, the coverage of chemisorbed oxygen, $\theta_0$, on clean iron films was found to be given by,

$$\theta_0 = 3 \cdot d \cdot (\delta R/R),$$

where the film thickness is in nanometers. This result is valid for coverage less than one-half monolayer and temperatures less than 450 K.

Detailed measurements of the film thickness and temperature dependence of the chemisorption-induced resistance change coupled with Auger electron spectroscopy measurements strongly support an origin for the resistance change involving direct charge transfer between the adsorbing species and the substrate atoms. Additional measurements from H$_2$, H$_2$S, and CO adsorption on iron films further support these results for the origin of the resistance change.

These studies also present a clear picture of chemisorption via an adsorbed molecular state and allow the investigation of variations in gas pressure on the appearance of the adsorption kinetics as well as insight on the kinetics for the formation of the initial oxide layer.

Specific information and results can be found in the published articles 1,4,6, and 14 listed in Section 5. Presentations related to this work are listed in Section 6 as follows: 3,5,7,13,20,27,36,37,51.

2.16 O$_2$:Titanium-Aluminum Alloys

Auger electron spectroscopy was used to measure the ambient temperature interaction of low pressure (2.7 x 10^{-6} N/m$^2$, 2 x 10^{8} Torr), gaseous oxygen with a series of titanium-aluminum alloys including the intermetallics, Ti$_3$Al, TiAl, and TiAl$_3$. Most of the alloys contained ternary additions.
The kinetics of the initial oxidation process was determined and the initial oxide overlayer and its growth mechanism characterized. Dissociation of the molecular oxygen appears to occur primarily on the titanium surface atoms, which also appear to control the oxidation process, even though the formation of the aluminum oxide would produce a greater energy gain.

From this study, the oxidation kinetics at low temperature for the titanium-aluminum alloys are shown to be determined primarily by the growth mechanisms for the bulk oxide scale (diffusion) and not by surface processes. The surface processes, in turn, appear to be dominated by the titanium surface atoms and not the aluminum surface atoms, at least in regard to the formation of the initial oxide layer, the precursor to the formation of the oxide scale.

Published articles relevant to the O₂:Titanium-Aluminum Alloys study are listed in Section 5 as follows: 5,13,14,22,23 with presentations listed in Section 6 as follows: 1,5,36,37,51,52. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.

2.2 Impurity Effects

Although the original goal of this program was to investigate the influence of several impurities on the kinetics for H₂ and H₂S chemisorption on iron, in fact it was possible to study only one surface impurity, namely oxygen. This limited work has produced several important observations involving not only the effect of surface impurities on chemisorption kinetics, but also the origin of the chemisorption-induced resistance change. In addition, it should be noted that the results outlined in section 2.16 above also relate to the effects of surface impurities on adsorption kinetics. Here, the surface impurity is a metallic component of the adsorption substrate and not just a surface metallic or non-metallic (covalent) grain boundary impurity.

2.21 H₂:O-Fe
The chemisorption-induced resistance change was utilized to determine the equilibrium and kinetics of H₂ adsorption into oxygen doped evaporated iron films. The chemisorption-induced resistance change has always been observed to be positive for simple adsorption onto a clean metal surface [4]. In the presence of adsorbed oxygen, however, a negative resistance change component appears. This can be seen in Fig. 1, which follows the time evolution of hydrogen adsorption onto an iron film surface doped with adsorbed oxygen.

The model developed to assume that the iron surface iron regions and regions which adsorbed oxygen. The resistance change originates normal regions of the film and chemisorption onto the assumed that equilibrium is hydrogen adsorbed in the two coverage in each region can be isotherm for dissociative change is then just the sum of region.

This model accurately describes the equilibrium isotherms and can be used to evaluate the dependence of temperature, oxygen coverage, and hydrogen coverage on the isotherm parameters. The model does not however provide any concert clue as to the origin of the negative component of the resistance change. It is also possible to characterize the adsorption kinetics with this model, where the kinetics for the positive component are assumed to relate to hydrogen adsorption on the normal surface. The kinetics of the negative component are similar to the positive component, but the rate is always less. This is illustrated in Fig. 1, where a model fit to the data is shown by the solid line. In this example, the kinetic rate for the negative component is about 10% smaller than for the positive component.

Based on this observation it is possible to make some statements about the effect of the adsorbed oxygen on the H₂ chemisorption rate constants. The variation of the low pressure H₂ adsorption rate with adsorbed oxygen coverage for the positive component is shown in Fig. 2. This should be representative of adsorption into the molecular precursor state. The pressure dependence of the H₂ adsorption rate for fixed oxygen coverage is shown in Fig. 3. Also shown in Fig. 3 is the measured
pressure dependence for a clean iron film showing that at high pressure the dissociative chemisorption of H₂ becomes rate limited.

The data in Fig. 2 are characteristic of an adsorption rate reduced by "site blocking." The shape of the data implies that the "site blocking" is not a simple one-for-one reduction mechanism. The data suggest that a single oxygen adatom influences a large number of adjacent empty adsorption sites. The results in Fig 3 are more interesting, because they imply that the presence of the adsorbed oxygen enhances adsorption by affecting the rate limiting adsorption step between the adsorbed molecular precursor state and the dissociated chemisorbed state [4]. On one hand, the presence of oxygen is reducing the adsorption rate into the molecular precursor (Fig. 2), while on the other hand, it is acting to increase the rate to go into the dissociated state (Fig. 3).

The published article relevant to the H₂:O-Fe study is listing 6 in Section 5 with presentations listed in Section 6 as follows: 12,13,14.
2.22 H₂S:O-Fe

Auger electron spectroscopy and the chemisorption-induced resistance change were utilized together to compare the kinetics of low pressure H₂S adsorption on clean and oxygen-covered iron films. The iron films were grown from a thermal vapor deposition source of high purity iron. The oxygen layer was formed by adsorbing oxygen to saturation coverage onto a clean iron film surface at about 295 K. The oxygen layer is nominally 1.5 to 2 monolayers thick. Although the oxygen overlayer does not affect the saturation coverage of adsorbed H₂S (which is estimated to be one-half a monolayer), it does significantly increase the adsorption rate. When compared with adsorption onto a clean iron surface, the pre-adsorbed oxygen increases the H₂S adsorption rate by a factor of about 2. The adsorption measurements were done at a constant gauge pressure of 6.4 × 10⁻⁵ N/m² (4.8 × 10⁻⁷ Torr). The adsorbed sulfur was observed to always resided on top of the oxygen layer.

Differences were found in the sulfur Auger spectrum obtained from the two surfaces. It is suggested that the differences observed in the adsorption rates and the shapes of the uptake curves result from a change in the rate-limiting adsorption step, from island growth for the clean iron surface to a molecular-precursor mediated adsorption on the oxygen-covered iron surface. The differences observed in the sulfur Auger spectrum are consistent with this view. In addition, the adsorption of H₂S did not lead to any obvious erosion of the oxygen overlayer at the measurement temperature.

The published articles relevant to the H₂S:O-Fe studies are listings 10 and 16 in Section 5, with presentations listed in Section 6 as follows: 10,11,12,33.

3.0 BULK TRANSPORT INVESTIGATIONS

3.1 Hydrogen/Deuterium Transport

The hydrogen (deuterium) permeation measurements were made using a “membrane” technique, where gaseous hydrogen (deuterium) at the entrance side is transported through the bulk of a thin membrane to the exit side. The permeation apparatus was constructed from ultra high vacuum components with the basic design of the apparatus patterned after the gas phase permeation apparatus of Nelson and Stein [8]. The permeation rate was determined under dynamic flow conditions where the exit volume was continuously evacuated at a constant pumping speed. For this experimental arrangement, the permeation flux was proportional to the partial pressure of the permeating gas in the exit volume. The partial pressure of the gas in the exit volume was measured with a quadrupole mass analyzer tuned to molecular hydrogen (deuterium). Absolute values for the rate were established by comparing the permeation rate signals with those from independently calibrated leak rate sources.

3.11 Incoloy 909

Hydrogen permeation measurements were made for Incoloy 909 [9]. Incoloy 909 is a high temperature alloy derived from the Ni-Fe-Co superalloy, Incoloy 903 and has been claimed to be more resistant to hydrogen degradation than Incoloy 903. In the present study, the hydrogen permeability, Φ, lattice diffusivity, D, and lattice solubility, S, were determined over the temperature range from 673 K (400°C) to 1083 K (810°C) and the pressure range from 2.7×10⁻⁵ N/m² (20 Torr) to 1.3×10⁵ N/m² (1000 Torr).
The hydrogen solubility was found to obey Sievert’s Law at all temperatures and pressures used in the study. The hydrogen permeability and diffusivity for Incoloy 909 are very similar to corresponding values obtained previously for Incoloy 903 [10]. If Incoloy 909 is more resistant to hydrogen degradation than Incoloy 903, it is not because of the significant differences in the lattice hydrogen transport parameters.

From the present measurements, the lattice hydrogen solubility in Incoloy 909 was found to be very weakly temperature dependent (a result of the small activation energy). This is an interesting result, as almost all Ni-Fe-Co alloys which have been studied appear to have strongly temperature dependent lattice solubilities. The measured hydrogen lattice transport parameters for Incoloy 909 are as follows:

\[
\Phi = 5.6 \times 10^{16} \exp \left( -51.1/RT \right), \frac{H_2}{m \cdot s \cdot \sqrt{N/m^2}}, \\
D = 1.2 \times 10^{-6} \exp \left( -51/RT \right), m^2/s, \text{ and} \\
S = 4.5 \times 10^{22} \exp \left( -0.1/RT \right), \frac{H_2}{m^3 \cdot \sqrt{N/m^2}},
\]

where \( T \) is the temperature in degrees Kelvin, \( R \) is the gas constant, and the activation energies are in units of kJ/mol.

Published articles relevant to the study of hydrogen transport in Incoloy 909 are listed in Section 5 as follows: 8,21,33, with presentations listed in Section 6 as follows: 31,45. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.

3.12 Mo-47.5Re

Hydrogen permeation measurements were made for Mo-47.5Re, a refractory metal alloy with good mechanical properties at elevated temperatures. In addition this alloy appears to be stable in the presence of hot hydrogen. For the present study, the deuterium permeability, \( \Phi \), lattice diffusivity, \( D \), and lattice solubility, \( S \), were determined over the temperature range from 613 K (340 C) to 1123 K (850 C) and the pressure range from \( 1.3 \times 10^3 \ N/m^2 \) (10 Torr) to \( 1.3 \times 10^5 \ N/m^2 \) (1000 Torr). Unlike the previous transport studies investigated in this agreement, deuterium, an isotope of hydrogen, was used in place of hydrogen because of the very low permeability of Mo-47.5Re. The very small level of permeating hydrogen was often masked by the hydrogen background present in the apparatus (residual outgassing from the walls of the apparatus).

The measured deuterium lattice transport parameters for Mo-47.5Re are as follows:

\[
\Phi = 9.8 \times 10^{15} \exp \left( -74.4/RT \right), \frac{D_2}{m \cdot s \cdot \sqrt{N/m^2}}, \\
D = 1.4 \times 10^{-4} \exp \left( -74.4/RT \right), m^2/s, \text{ and} \\
S = 7.2 \times 10^{19} \exp \left( -(0.0 \pm 7.3)/RT \right), \frac{D_2}{m^3 \cdot \sqrt{N/m^2}},
\]

where \( T \) is the temperature in degrees Kelvin, \( R \) is the gas constant, and the activation energies are in units of kJ/mol.

Published articles relevant to this study of deuterium transport in Mo-47.5Re are listed in Section 5 as follows: 9,21,33, with presentations listed in Section 6 as follows: 29,31,45. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.
3.13 Haynes 188

Hydrogen permeation measurements were made for Haynes 188 [11]. Haynes 188 is a high temperature Co-Cr-Ni-W based superalloy that is claimed to be highly resistant to hydrogen degradation. In the present study, the hydrogen permeability, $\Phi$, lattice diffusivity, $D$, and lattice solubility, $S$, were determined over the temperature range from 490 K (217 °C) to 1150 K (877 °C) and the pressure range from $1.3 \times 10^3$ N/m$^2$ (10 Torr) to $1.3 \times 10^5$ N/m$^2$ (1000 Torr).

The measured hydrogen lattice transport parameters for Haynes 188 are as follows:

$$\Phi = 2.4 \times 10^{17} \exp \left(\frac{-64.6}{RT}\right), \frac{H_2}{m \cdot s \cdot \sqrt{N/m^2}},$$

$$D = 4.6 \times 10^7 \exp \left(\frac{-42.3}{RT}\right), \frac{m^2}{s}, (T>690 K), and$$

$$S = 5.2 \times 10^{23} \exp \left(\frac{-21.3}{RT}\right), \frac{H_2}{m^3 \cdot \sqrt{N/m^2}} (T>690 K),$$

where $T$ is the temperature in degrees Kelvin, $R$ is the gas constant, and the activation energies are in units of kJ/mol.

Published articles relevant to this study of hydrogen transport in Haynes 188 are listings 11 and 21 in Section 5 with presentations listed in Section 6 as follows: 31, 34. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.

3.2 Modeling of Bulk Transport with Surface Reactions

Model calculations were made of the effect that surface reactions might have on the interpretation of gas phase permeation measurements used to determine hydrogen transport parameters in iron (and nickel). The model utilized the surface reactions determined for the H$_2$:Fe system (section 2.11) combined with simple Fickian diffusion inside the permeation membrane. The coupled non-linear equations describing the complete transport model were reduced to difference equations and solved by numerical methods. The computations show that the model correctly predicts the experimental observations when the correct boundary conditions for the hydrogen surface reaction are used. Anomalies observed in the original measurement, however, had been ascribed to interactions between the dissolved protonic-hydrogen and bulk traps [8]. For the H$_2$:Fe system, the model calculation clearly shows that the significance of bulk traps must be reevaluated, since their effect on the transport process can be easily replicated by the established surface chemisorption processes.

Published articles relevant to the modeling studies are listed in Section 5 as follows: 3, 15, 18 with presentations listed in Section 6 as follows: 4, 6, 9, 17, 28.

4.0 OTHER

4.1 Hydrogen Test Facilities Survey and Summary

Characterizing material behavior and testing for possible degradation of mechanical properties in the appropriate hydrogen environment is an important activity in the development of any advanced hydrogen powered rocket propulsion system, such as was envisioned for the National Aero-Space Plane (NASP). To facilitate in preparing for testing activities in the NASP program, a survey was initiated in 1989 of existing and planned facilities capable of testing for mechanical property degradation in high pressure, high temperature hydrogen environment. The initial survey request was distributed to government laboratories, industrial laboratories, private testing laboratories, and
universities known to be engaged in this type of work. Additional input was received from other laboratories as their presence became known.

The last update to this survey, which was done in 1992, is presented in Appendix A of this report. Collectively, the facilities listed in this summary have the ability to test in hydrogen environments with temperatures ranging from 18 K (liquid hydrogen, -255 C) to 3,050 K (2778 C) and for pressures ranging up to $2 \times 10^8$ N/m$^2$ (1.5 x 10$^6$ Torr).

Published articles relevant to this survey are listings 31 and 32 in Section 5 the presentation listing, 24, in Section 6. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.

5.0 PUBLICATIONS

6.1 Journal Publications


6.2 In Books


6.3 Government Publications


### 6.0 PRESENTATIONS

#### 5.1 Professional Meetings


3. Origin of the Chemisorption-Induced Resistance Change for O2 and H2S Adsorbed onto Fe Films, contributed presentation, 8th International Vacuum Congress, 4th International...


15. Surface Characterization by AES and EELS of Ti₃Al and TiAl (with M. Ownbey), contributed presentation, AIME-TMS Fall Meeting, Cincinnati, Ohio (1987).


5.2 Program Reviews


39. Characterization of Ti3Al and Hydrogen Charged Ti3Al by AES and EELS - Preliminary Results, presentation to representatives of the Joint Program Office for the National Aero-Space Plane, Wright-Patterson AFB, Ohio; Moffett Field, California (1987).


5.3 Other

46. Adsorption of H$_2$S onto (111) Oriented Fe Films at 300K, invited seminar, University of Munich, Munich, Germany (1980).

47. Changes in the Desorption Rate Near the Curie Temperature for H$_2$ Chemisorbed onto Ni Films, invited seminar, Institut fur Kernforschungsanlage Julich GmbH, Julich, Germany (1980).

48. Adsorption of H$_2$S onto (111) Oriented Fe Films at 300K, invited seminar, University of California, Santa Barbara, California (1981).


51. The Chemisorption-Induced Resistance Change and It's Application in Determining H$_2$:Fe Chemisorption Kinetics, invited seminar, University of California, Davis, California (1985).

52. The Isothermal Kinetics of H$_2$ Chemisorption onto Fe Films Determined with the Chemisorption-Induced Resistance Change, invited seminar, Sandia National Laboratories, Albuquerque, New Mexico (1985).

7.0 STUDENT PARTICIPATION

Several students have participated directly in the work of this program. These were undergraduate students participating in the Cooperative Work Experience Program operated jointly by the Foothill-DeAnza Community College District and NASA-Ames Research Center. The program allowed students to acquire practical experience in areas of their vocational interest. The following students worked in this program:

1. Adel Taslimi 1979-1980
2. Debra Rees 1981
3. Loan Nguyen 1982-1983
5. Ernesto Godinez 1985
8. Mark Ownbey (Senior Associate Program) 1987
9. James Prunty 1987
10. Kevin Sidensol 1989

Students supervised under programs other than the Cooperative Work Experience Program:
1. Bruce Alston 1984
   Co-op Program with North Carolina A&T State University

2. Bryant S. Rayngay 1988
   Internship program with Bennington College.

8.0 REFERENCES


9. "Incoloy" is a trademark of Inco Alloys International, Huntington, West Virginia.


Appendix A

Summary of 1992 Hydrogen Test Facilities Survey

For each organization participating in the survey, a contact person has been indicated. Inquiries concerning testing at a particular facility should be addressed to the contact person.