FINAL TECHNICAL REPORT

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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 it's influence on material properties.

2.11 H_2: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/m^2 (8×10^{-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 H_2: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.

2.12

<u>H₂:Be</u>

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 3×10^{-3} N/m² (2.3×10^{-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 4×10^{-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 H₂: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 H₂: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_3Al, $TiAl$, and $TiAl_3$.

The surface hydrogen was derived from two sources; (1) dissociative adsorption of H₂ at low pressure (6.6×10^{-3} N/m², 5×10^{-5} 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 (1×10^{5} N/m²) hydrogen environment. Pre-charging can produce bulk hydride phases in these alloys, especially the Ti_3Al 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 obtain with preadsorbed hydrogen.

Published articles relevant to the H₂: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 H₂S:Fe

Work to understand the chemisorption kinetics of H₂S 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 H₂S is known to be significantly more aggressive in embrittling iron alloys than gaseous H₂ alone. Since it has been determined that the H₂ 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 H₂S molecule may explain the enhanced embrittlement rate observed with H₂S. Use of H₂S is also a standard procedure for doping a sulfur onto a clean surface.

The kinetics of H_2S 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_2S 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_2S adsorption onto iron was essentially equal to that for H_2 adsorption onto iron under similar conditions.

Published articles relevant to the H_2S: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, θ_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_2S, 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 (2.7×10^{-6} N/m^2, 2×10^{-8} Torr), gaseous oxygen with a series of titanium-aluminum alloys including the intermetallics, Ti_3Al, TiAl, and $TiAl_3$. Most of the alloys contained ternary additions.

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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.
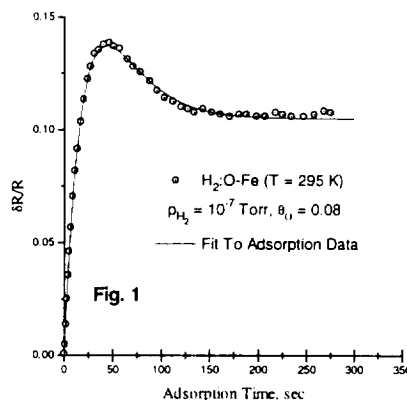
Published articles relevant to the O_2:Titanium-Aluminum Alloys study are listed in Section 5 as follows: 5,13,14,22,23 with presentations listed in Section 6 as follows: 1,5,36,37,51,52. This work was undertaken as part of the NASP-Hydrogen Materials Compatibility Program.

2.2 Impurity Effects

Although the original goal of this program was to investigate the influence of several impurities on the kinetics for H_2 and H_2S 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 H_2:O-Fe

The chemisorption-induced resistance change was utilized to determine the equilibrium and kinetics of H_2 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.

Fig. 1

The model developed to describe this phenomenon consists of normal ("clean") iron regions and regions which are modified by presence of the adsorbed oxygen. The positive component to the total resistance change originates from chemisorption onto the normal regions of the film and the negative component from chemisorption onto the oxygen-modified regions. It is assumed that equilibrium is established between the hydrogen adsorbed in the two regions and that the hydrogen coverage in each region can be described by a Langmuir isotherm for dissociative adsorption. The total resistance change is then just the sum of the resistance changes for each 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.
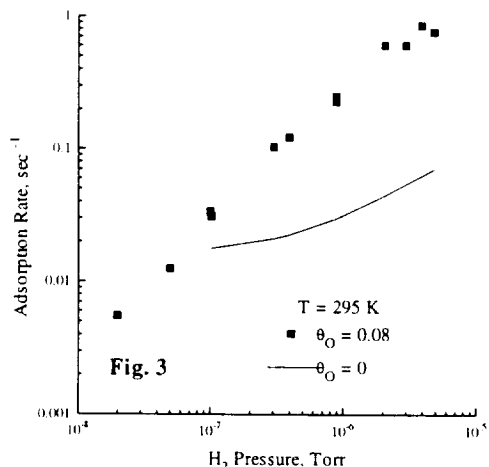
Based on this observation it is possible to make some statements about the effect of the adsorbed oxygen on the H_2 chemisorption rate constants. The variation of the low pressure H_2 adsorption rate with adsorbed oxygen coverage for the positive component is shown in Fig. 2. This should be representative of adsorption into the molecular precursor state. The pressure dependence of the H_2 adsorption rate for fixed oxygen coverage is shown in Fig. 3. Also shown in Fig. 3 is the measured

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pressure dependence for a clean iron film showing that at high pressure the dissociative chemisorption of H_2 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 H_2:O-Fe study is listing 6 in Section 5 with presentations listed in Section 6 as follows: 12,13,14.

Fig. 3

T = 295 K
■ $\theta_O = 0.08$
—— $\theta_O = 0$

H_2 Pressure, Torr

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<u>2.22 H$_2$S:O-Fe</u>

Auger electron spectroscopy and the chemisorption-induced resistance change were utilized together to compare the kinetics of low pressure H$_2$S 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 H$_2$S (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 H$_2$S adsorption rate by a factor of about 2.* The adsorption measurements were done at a constant gauge pressure of 6.4 x 10^{-5} N/m^2 (4.8 x 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 up-take 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 H$_2$S did not lead to any obvious erosion of the oxygen overlayer at the measurement temperature.

The published articles relevant to the H$_2$S: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.

<u>3.11 Incoloy 909</u>

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 2.7x10^3 N/m^2 (20 Torr) to 1.3x10^5 N/m^2 (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:

$$\Phi = 5.6 \times 10^{16} \exp(-51.1/RT), \, H_2/m \cdot s \cdot \sqrt{N/m^2},$$

$$D = 1.2 \times 10^{-6} \exp(-51/RT), \, m^2/s, \text{ and}$$

$$S = 4.5 \times 10^{22} \exp(-0.1/RT), \, H_2/m^3 \, \sqrt{N/m^2},$$

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, Φ, 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 1.3×10^3 N/m^2 (10 Torr) to 1.3×10^5 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 permeablity 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:

$$\Phi = 9.8 \times 10^{15} \exp(-74.4/RT), \, D_2/m \cdot s \cdot \sqrt{N/m^2},$$

$$D = 1.4 \times 10^{-4} \exp(-74.4/RT), \, m^2/s, \text{ and}$$

$$S = 7.2 \times 10^{19} \exp(-(0.0 \pm 7.3)/RT), \, D_2/m^3 \cdot \sqrt{N/m^2},$$

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.

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, Φ, 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 1.3×10^3 N/m^2 (10 Torr) to 1.3×10^5 N/m^2 (1000 Torr).

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

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

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

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

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 2×10^8 N/m^2 (1.5×10^6 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

1. Origin of the Chemisorption-Induced Resistance Change for O_2 Adsorbed onto Fe (with Jo Wilcox), in *Proceedings of the Eighth International Vacuum Congress* (Cannes, France) 1980 (Supplement a la Revue, *Le Vide, les Couches Minces*, No. 201), Vol. 1, p. 750.

2. Kinetics of H_2S Adsorption onto Fe Surfaces, in *Proceedings of the Fourth International International Conference on Solid Surfaces and the Third European Conference on Surface Science* (Cannes, France) 1980 (Supplement a la Revue, *Le Vide, les Couches Minces*, No. 201), Vol. 1, p. 494.

3. Influence of H_2 Chemisorption Kinetics on the Interpretation of Hydrogen Transport through Iron Membranes (with A. Taslimi and H. G. Nelson), *Scripta Met.* 15(1981)929.

4. Observation of an Excess Current Noise Resulting from Oxygen Adsorption onto Iron Films (with Jo Wilcox and H. G. Nelson), *J. Vac. Sci. Technol.* 20(1982)898.

5. The Isothermal Kinetics of Hydrogen Adsorption onto Iron Films Observed with the Chemisorption-Induced Resistance Change, *Surface Science* 150(1985)451.

6. Influence of Preadsorbed Oxygen on the Sign and Magnitude of the Chemisorption-Induced Resistance Change for H_2 Adsorption onto Fe Films, *J. Vac. Sci. Technol.* A4(1986)623.

7. The Initial Oxidation of Alpha-2 (Ti_3Al) and Gamma (TiAl) Titanium Aluminide Alloys, *Materials Science and Engineering*, A153(1992)608.

8. Gas Phase Hydrogen Permeation in a Ni-Fe-Co Superalloy, *Scripta Metallurgica et Materialia*, 8(1993)1143.

9. Diffusivity and Solubility of Deuterium in a Mo-Re Alloy, *Scripta Metallurgica et Materialia*, 30(1994)749.

10. H_2S Adsorption onto Clean and Oxygen Covered Iron Films (with R.D. Moorhead), *Surface Science*, 365(1996)614.

11. Hydrogen Transport Parameters for a Cobalt Based Alloy, *Journal of Alloys and Compounds*, 253-254(1997)381.

12. Comparative Study of the Initial Oxidation of $Ti_{1-x}Al_x$ Alloys, accepted for publication in *Applied Surface Science*.

6.2 In Books

13. Comparison of Adsorption Kinetics on Iron of H_2 and H_2S, in *Hydrogen Effects in Metals*, J. M. Bernstein and A. W. Thompson, eds. (The Metallurgical Society of AIME, Warrendale, Pennsylvania) 1981, p. 135.

14. The Chemisorption-Induced Resistivity Change and its Application to Determining H_2:Fe Chemisorption Kinetics, in *Advanced Techniques for Characterizing Hydrogen in Metals*, N. F. Fiore and B. J. Berkowitz, eds. (The Metallurgical Society of AIME, Warrendale, Pennsylvania) 1982, p. 155.

15. The Anomalous Diffusivity of Hydrogen in Iron Interpreted as a Surface Process (with H. G. Nelson), in *Proceedings of the Ninth International Vacuum Congress and Fifth International Conference on Solid Surfaces*, J. L. de Segovia, ed. (Madrid, Spain) 1983, p. 62.

16. The Sequential Adsorption of H_2S and O_2 onto Fe Films (with R. Dale Moorhead), in *Proceedings of the Ninth International Vacuum Congress and Fifth International Conference on Solid Surfaces*, J. L. de Segovia, ed. (Madrid, Spain) 1983, p. 75.

17. Characterization of Hydrogen Interactions with the Surface of Alpha-2 titanium Aluminide Alloys, in *Hydrogen Effects on Material Behavior*, N. R. Moody and A. W. Thompson, eds. (The Minerals, Metals, and Materials Society, Warrendale, Pennsylvania) 1990, p. 507.

18. The Modeling of Gas Phase Permeation Through Iron and Nickel Membranes (with David K. Kuhn), in *Hydrogen Effects on Material Behavior*, N. R. Moody and A. W. Thompson, eds. (The Minerals, Metals, and Materials Society, Warrendale, Pennsylvania) 1990, p. 33.

19. A Study of the Interaction of Hydrogen with the Surface of Titanium-Aluminum Intermetallic Alloys, in *Proceedings of the Third International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications*, D. Noréus, S. Rundqvist, and E. Wicke, eds. (R. Oldenbourg Verlag, München) 1994, p.1016.

20. Hydrogen Solubility in Ti-24Al-11Nb (with S.N. Sankaran and A.W. Thompson), in *Hydrogen Effects in Materials*, A.W. Thompson and N.R. Moody, eds. (The Minerals, Metals & Materials Society, Warrendale, PA) 1996, p. 215.

21. Comparison of Lattice Hydrogen Transport Parameters for the High Temperature Alloys, Incoloy 909, Haynes 188, and Mo-47.5Re, in *Hydrogen Effects in Materials*, A.W. Thompson and N.R. Moody, eds. (The Minerals, Metals & Materials Society, Warrendale, PA) 1996, p. 243.

6.3 Government Publications

22. An Investigation of the Kinetics of Hydrogen Chemisorption on Iron Metal Surfaces, NASA Contractor Report 166,323, April 1982.

23. Surface Reaction Kinetics: Hydrogen Chemisorption, in NASA Technical Memorandum 86662, *Research and Technology Annual Report 1984* (NASA-Ames Research Center, Moffett Field, California) 1985.

24. *Summary Proceedings of the Workshop on Hydrogen-Material Interactions*, ed. (with H. G. Nelson), National Aero-Space Plane Workshop Publication 1001 (NASP Joint Program Office, Wright-Patterson AFB, Ohio) 1987.

25. Hydrogen-Materials Compatibility: Potential Problems and Possible Solutions (with H. G. Nelson and T. L. Panontin), in *Proceedings of the Third National Aero-Space Plane Technology Symposium* (NASA-Langley Research Center, Langley, Virginia) 1987.

26. Surface Characterization of Hydrogen Charged and Uncharged Alpha-2 and Gamma Titanium Aluminide Alloys Using AES and REELS, in *Summary Proceedings of the Third Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1007, H. G. Nelson, ed. (NASP Joint Program Office, Wright-Patterson AFB, Ohio) 1990, p. 105.

27. Qualitative Behavior of an SCS-6/Ti-15-3 Metal Matrix Composite in a Low Pressure Hydrogen Environment (with H.G. Nelson and T.L. Panotin), in *Summary Proceedings of the Third Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1007, H. G. Nelson, ed. (NASP Joint Program Office, Wright-Patterson AFB, Ohio) 1990, p. 205.

28. Development of Gaseous Hydrogen Barrier Coatings for High Temperature NASP Metallic Materials - Problems and Challenges (with Abdus S. Khan), in *Proceedings of the Eighth National Aero-Space Plane Technology Symposium* (NASA Langley Research Center, Langley, Virginia) 1990, Volume IV-Materials, p. 107.

29. An Investigation of Hydrogen Adsorption on Beryllium, in *Summary Proceedings of the Fourth Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1013, H. G. Nelson, ed. (Langley Research Center, February, 1993), p. 307.

30. Development of Gaseous Hydrogen Barrier Coatings for High Temperature NASP Metallic Materials: Problems and Challenges (with Abdus S. Khan), in *Summary Proceedings of the Fourth Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1013, H. G. Nelson, ed. (Langley Research Center, February, 1993), p. 267.

31. Facilities for Mechanical Property Testing in Gaseous Hydrogen, in *Second Workshop on Hydrogen Effects on Materials in Propulsion Systems*, B.N. Bhat, R.L. Dreshfield, and E.J. Vesely, Jr., eds., NASA Conference Publication 3182, 1992, p.12.

32. Hydrogen Materials Testing for Generic Hypersonic Engines and a Survey of National Facilities (with H.G. Nelson), to be published in the *Proceedings of the Workshop on Hydrogen Corrosion in Nuclear Thermal Propulsion Reactors*, Albuquerque, New Mexico, January 9, 1993.

33. Hydrogen (D_2) Permeation in INCO 909 and Mo-Re Alloys: Preliminary Results, in *Summary Proceedings of the 5th Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1014, H.G. Nelson, ed. (NASA-Ames Research Center, Aprill, 1994) p. 379.

6.0 PRESENTATIONS

5.1 Professional Meetings

1. A Comparison of Adsorption Kinetics on Iron of H_2 and H_2S, contributed presentation, Third International Conference on the Effect of Hydrogen on the Behavior of Materials, Jackson Lake Lodge, Wyoming (1980).

2. Adsorption of H_2S onto (111) Oriented Fe Films at 300K, contributed presentation, 8th International Vacuum Congress, 4th International Conference on Solid Surfaces, and the 3rd European Conference on Surface Science, Cannes, France (1980).

3. Origin of the Chemisorption-Induced Resistance Change for O_2 and H_2S Adsorbed onto Fe Films, contributed presentation, 8th International Vacuum Congress, 4th International

Conference of Solid Surfaces, and 3rd European Conference of Surface Science, Cannes, France (1980).

4. Influence of Surface Adsorption States on Gas Phase H_2 Transport through Iron, contributed presentation, March Meeting of the American Physical Society, Phoenix, Arizona (1981).

5. The Chemisorption-Induced Resistivity Change and its Application to Determining H_2:Fe Chemisorption Kinetics, invited presentation, Fall Meeting, The Metallurgical Society of AIME, Louisville, Kentucky (1981).

6. Influence of Hydrogen Chemisorption Kinetics in the Interpretation of Hydrogen Transport through Iron Membranes, contributed presentation, Fall Meeting, The Metallurgical Society of AIME, Louisville, Kentucky (1981).

7. Observation of an Excess Current Noise Resulting from Oxygen Adsorption onto Iron Films, contributed presentation, 28th National Symposium of the American Vacuum Society, Anaheim, California (1981).

8. H_2S Adsorption Kinetics on Fe Films, invited presentation, Spring Meeting of the California Catalysis Society, Pleasanton, California (1982).

9. The Anomalous Diffusivity of Hydrogen in Iron Interpreted as a Surface Process, contributed presentation, 9th International Vacuum Congress and 5th International Conference on Solid Surfaces, Madrid, Spain (1983).

10. The Sequential Adsorption of H_2S and O_2 onto Fe Films, contributed presentation, 9th International Vacuum Congress and 5th International Conference on Solid Surfaces, Madrid, Spain (1983).

11. Influence of Preadsorbed Oxygen on the Adsorption of H_2S on Fe, contributed presentation, Sixth Symposium on Applied Surface Analysis, Dayton, Ohio (1984).

12. Enhancement of H_2 and H_2S Adsorption on Fe by Adsorbed Oxygen, contributed presentation, AIME-TMS Fall Meeting, Toronto, Canada (1985).

13. Influence of Oxygen Impurities on the Sign and Magnitude of the Resistance Change for H_2 Chemisorbed onto Fe Films, contributed presentation, 32nd National Symposium of the American Vacuum Society , Houston, Texas (1985).

14. Initial Sticking Coefficient of Hydrogen Adsorption onto Fe Films Predosed with Oxygen, contributed presentation, 14th DOE Surface Studies Conference, Albuquerque, New Mexico (1987).

15. Surface Characterization by AES and EELS of Ti_3Al and TiAl (with M. Ownbey), contributed presentation, AIME-TMS Fall Meeting, Cincinnati, Ohio (1987).

16. Intrinsic Effect of Dosing Procedures on the Interpretation of Precursor Mediated Adsorption (with Linda Bell), contributed presentation, 34th National Symposium of the American Vacuum Society, Anaheim, California (1987).

17. The Modeling of Gas Phase Permeation through Iron and Nickel Membranes (with David K. Kuhn), contributed presentation, Fourth International Conference on the Effects of Hydrogen on Material Behavior, Jackson Lake Lodge (1989).

18. Characterization of Hydrogen Interactions with the Surface of Alpha-2 Titanium Aluminide Alloys, contributed presentation, Fourth International Conference on the Effects of Hydrogen on Material Behavior, Jackson Lake Lodge (1989).

19. An Investigation of Hydrogen Interactions at the Surface of Titanium-Aluminum Intermetallic Alloys, contributed presentation, 12th Symposium on Applied Surface Analysis, Albuquerque, New Mexico (1990).

20. Observation of a Maximum in the Coverage Dependence of the Sticking Coefficient for O_2 Chemisorption onto Fe Films, contributed presentation, 11th European Conference on Surface Science, Salamanca, Spain (1990).

21. The Initial Surface Oxidation of Alpha-2 and Gamma Titanium Aluminide Alloys, contributed presentation, International Conference on High Temperature Aluminides and Intermetallics, San Diego, California (1991).

22. Coverage Dependence of the Sticking Coefficient for CO Adsorption onto Evaporated Fe Films and The Effect of Substrate Temperature, contributed presentation, 38th National Symposium of the American Vacuum Society , Seattle, Washington (1991).

23. Comparative Study of Oxygen Chemisorption onto a Series of $Ti_{1-x}Al_x$ Structural Alloys, contributed presentation, The 28th Symposium of the New Mexico Chapter of the American Vacuum Society, Albuquerque, New Mexico (1992).

24. Testing in a Hydrogen Environment and Survey of National Test Facilities, invited presentation, The 1992 Conference on Advanced Earth-to-Orbit Propulsion Technology, Marshall Space Flight Center, Huntsville, Alabama (1992).

25. Hydrogen Interactions at the Surface of Titanium-Aluminum Intermetallic Alloys, contributed presentation, International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications, Uppsala, Sweden (1992).

26. Hydrogen Materials Testing for Generic Hypersonic Engines and a Survey of National Facilities, invited presentation (with H.G. Nelson), Workshop on Hydrogen Corrosion in Nuclear Thermal Propulsion Reactors, Albuquerque, New Mexico (1993).

27. Coverage Dependence of the Sticking Coefficients for CO, O_2, and H_2S Adsorption onto Evaporated Fe Films, contributed presentation, 29th Annual Symposium of the New Mexico Chapter of the American Vacuum Society and the eighteenth Department of Energy Surface Studies Conference, Santa Fe, New Mexico (1993).

28. A Specific Model for Hydrogen Transport through Iron Membranes Including Surface Reactions, contributed presentation, Gordon Research Conference on Hydrogen-Metal Systems, Tilton, New Hampshire (1993).

29. Parameters for Deuterium Transport in Mo-47.5Re, contributed presentation, AIME-TMS Fall Meeting, Pittsburgh, Pennsylvania (1993).

30. Hydrogen Solubility in Ti-24Al-11Nb, invited presentation, Fifth International Conference on Hydrogen Effects on Material Behavior, Jackson Lake Lodge, Wyoming (1994).

31. Comparison of Lattice Hydrogen Transport Parameters of the High Temperature Alloys, Incoloy 909, Haynes 188, and Mo-47.5Re, Fifth International Conference on Hydrogen Effects on Material Behavior, Jackson Lake Lodge, Wyoming (1994).

32. Hydrogen Solubility in an α-2 Titanium Aluminide Alloy, contributed presentation, Gordon Research Conference on Hydrogen-Metal Systems, New England College, Henniker, New Hampshire (1995).

33. Effect of Oxygen on the Kinetics for H_2S Adsorption onto Iron, invited presentation, Metal-Hydrogen Systems Symposium, American Chemical Society Regional Meeting, Dayton, Ohio (1996).

34. Hydrogen Transport Parameters for a Cobalt Based Alloy, contributed presentation, International Symposium on Metal Hydrogen Systems, Les Diablerets, Switzerland (1996).

35. Comparative Study of the Initial Oxidation of $Ti_{1-x}Al_x$ Alloys, contributed presentation, Sixteenth European Conference on Surface Science, Genova, Italy (1996).

36. Characterization of the Resistance Change Produced by H_2, H_2S, CO, and O_2 Chemisorption onto Evaporated Iron Films, contributed presentation, Tenth International Conference on Thin Films, Salamanca, Spain (1996).

37. Characterization of the Resistance Change Produced by H_2, H_2S, CO, and O_2 Chemisorption onto Evaporated Iron Films, contributed presentation, 43rd National Symposium of the American Vacuum Society, Philadelphia, Pennsylvania (1996).

5.2 Program Reviews

38. Hydrogen-Materials Compatibility: Potential Problems and Possible Solutions (with H. G. Nelson and T. L. Panontin), invited presentation, Third National Aero-Space Plane Technology Symposium, Moffett Field, California (1987).

39. Characterization of Ti_3Al and Hydrogen Charged Ti_3Al 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).

40. Surface Hydrogen Interactions with Alpha-2 and Gamma Titanium Aluminide Alloys Observed with AES and REELS, contributed presentation, Third NASP Workshop: Hydrogen-Material Interactions, Scottsdale, Arizona (1989).

41. Qualitative Behavior of an SCS_6/Ti-15-3 Metal Matrix Composite in a Low Pressure Hydrogen Environment (with H. G. Nelson and T. L. Panontin), contributed presentation, Third NASP Workshop: Hydrogen-Materials Interactions, Scottsdale, Arizona (1989).

42. Development of Gaseous Hydrogen Barrier Coatings for High Temperature NASP Metallic Materials - Problems and Challenges (with Abdus Khan), invited presentation, Eight National Aero-Space Plane Technology Symposium, Monterey, California (1990).

43. An Investigation of Hydrogen Adsorption on Beryllium, contributed presentation, Fourth NASP Workshop: Hydrogen-Material Interactions, Scottsdale, Arizona (1990).

44. Development of Gaseous Hydrogen Barrier Coatings for High Temperature NASP Metallic Materials - Problems and Challenges (with Abdus Khan), invited presentation, Fourth NASP Workshop: Hydrogen-Material Interactions, Scottsdale, Arizona (1990).

45. Hydrogen (D_2) Permeation in INCO 909 and Mo-Re Alloys: Preliminary Results, contributed presentation, Fifth Workshop on Hydrogen-Material Interactions, Phoenix, Arizona (1992).

5.3 Other

46. Adsorption of H_2S 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 Kernoforschungsanlage Julich GmbH, Julich, Germany (1980).

48. Adsorption of H_2S onto (111) Oriented Fe Films at 300K, invited seminar, University of California, Santa Barbara, California (1981).

49. Influence of Hydrogen Chemisorption Kinetics on the Interpretation of Hydrogen Transport through Iron Membranes, invited seminar, Sandia National Laboratories, Livermore, California (1982).

50. Common Surface Analysis Techniques, An Overview, invited seminar, San Jose State University, San Jose, California (1983).

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
4. Mark Ownbey   1984-1985
5. Ernesto Godinez   1985
6. Ken Kunzel   1985-1986
7. Michael O'Connell   1986-1987
8. Mark Ownbey (Senior Associate Program) 1987
9. James Prunty   1987
10. Kevin Sidensol   1989
11. Kevin Haralson   1990-1991
12. James Park   1991-1992

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

1. H. G. Nelson, in *Treatise on Materials Science and Technology, Embrittlement of Engineering Alloys*, C. L.Briant and S. K. Banerji, eds. (Academic Press, New York, 1983), vol. 25, p. 344.

2. H. G. Nelson, D. P. Williams, and A. S. Tetelman, *Metall. Trans.* 2(1971)953.

3. *Chemisorption of Gases on Metals*, F.C. Tompkins (Academic Press, New York, 1978).

4. M. R. Shanabarger, in *Hydrogen Effects in Metals,* J.M. Bernstein and A.W. Thompson, eds (The Metallurgical Society of AIME, Warrendale, Pennsylvania, 1981), p. 135.

5. Advanced Materials to Fly High in NASP, T. M. F. Ronald, *Advanced Materials and Processes* 135(May, 1989)29.

6. *Summary Proceedings of the Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1001, H.G. Nelson and M.R. Shanabarger, eds., (NASP Joint Program Office, Wright-Patterson AFB, Ohio,1987).

7. M. R. Shanabarger, in *Second Workshop on Hydrogen Effects on Materials in Propulsion Systems*, B.N. Bhat, R.L. Dreshfield. and E.J. Vesely, Jr., eds., NASA Conference Publication 3182, 1992, p.12.

8. *Gas Phase Hydrogen Permeation through Alpha Iron, 4130 Steel, and 304 Stainless Steel from less than 100 C to Near 600 C*, NASA Technical Note, NASA TN D-7265, H.G. Nelson and J.E. Stein (NASA, Washington, DC, 1973).

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

10. W.M. Robertson, Metall. Trans., 8A, 1709 (1977).

11. "Haynes 188" is a trademark of Haynes International, Inc., Kokomo, Indiana.

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.