

(NASA-TM-86479) AN ELECTROCHEMICAL STUDY OF
HYDROGEN UPTAKE AND ELIMINATION BY BARE AND
GOLD-PLATED WASPALLOY (NASA) 28 P
HC A03/MF A01

N85-11222

CSSL 11F

Unclass
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NASA Technical Memorandum

NASA TM -86479

AN ELECTROCHEMICAL STUDY OF HYDROGEN
UPTAKE AND ELIMINATION BY BARE AND
GOLD-PLATED WASPALLOY

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and James R. Lowery

Materials and Processes Laboratory

October 1984



National Aeronautics and
Space Administration

George C. Marshall Space Flight Center

1. REPORT NO. NASA TM -86479		2. GOVERNMENT ACCESSION NO.		3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE An Electrochemical Study of Hydrogen Uptake and Elimination by Bare and Gold-Plated Waspaloy				5. REPORT DATE October 1984	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Merlin D. Danford, Gordon E. DeRamus, Jr., and James R. Lowery				8. PERFORMING ORGANIZATION REPORT #	
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812				10. WORK UNIT NO.	
				11. CONTRACT OR GRANT NO.	
				13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum	
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES Prepared by Materials and Processes Laboratory.					
16. ABSTRACT <p>Two electrochemical methods for the determination of hydrogen concentrations in metals are discussed and evaluated. The take-up of hydrogen at a pressure of 5,000 psi by Waspaloy metal was determined experimentally at 24°C. It was found that the metal becomes saturated with hydrogen after an exposure time of about 1 hr. For samples charged with hydrogen at high pressure, most of the hydrogen is contained in the interstitial solid solution of the metal. For electrolytically charged samples, most of the hydrogen is contained as surface and subsurface hydrides. Hydrogen elimination rates were determined for these two cases, with the rate for electrolytically charged samples being greater by over a factor of two. Theoretical effects of high temperature and pressure on hydrogen take-up and elimination by bare and gold plated Waspaloy metal was considered. The breakthrough point for hydrogen at 5,000 psi, determined experimentally, lies between a gold thickness of 0.0127 mm (0.0005 in.) and 0.0254 mm (0.001 in.) at 24°C.</p> <p>Electropolishing was found to greatly reduce the uptake of hydrogen at high pressure by Waspaloy metal at 24°C. Possible implications of the results obtained in this study, as they apply to the turbine disk of the Space Shuttle Main Engine, are discussed.</p>					
17. KEY WORDS			18. DISTRIBUTION STATEMENT Unclassified - Unlimited		
19. SECURITY CLASSIF. (of this report) Unclassified		20. SECURITY CLASSIF. (of this page) Unclassified		21. NO. OF PAGES 26	22. PRICE NTIS

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TECHNICAL MEMORANDUM

AN ELECTROCHEMICAL STUDY OF HYDROGEN UPTAKE AND ELIMINATION BY BARE AND GOLD-PLATED WASPALOY

INTRODUCTION

This study was directed toward gaining information that might be useful in connection with problems associated with the turbine disks of the Space Shuttle Main Engine, as well as to investigate and develop electrochemical methods for determining hydrogen concentrations in metals. It has been known for some time that Waspaloy metal, the material which is useful for the turbopump disks, is subject to hydrogen environment embrittlement. Fatigue and fracture toughness studies have indicated that a hydrogen environment contributes strongly to a reduction in mechanical properties of the Waspaloy metal. To alleviate this problem, the turbine disks are gold plated to a thickness of 0.127 mm (0.005 in.) or more, which supposedly prevents the penetration of hydrogen into the Waspaloy metal. The thickness of gold plating necessary to prevent hydrogen embrittlement, based on reduction in area in smooth tensile tests, has been determined to be 0.041 mm (0.0016 in.). The specified plating thickness on the turbine disk, as set forth in the specifications, lies between 0.051 mm (0.002 in.) and 0.127 mm (0.005 in.). However, problems have been encountered with the gold plating in that the gold plating on the downstream face of the fir tree slot area is often lost in service. This debonding has been attributed [1] to stresses which exceed the bond strength between the gold plating and Waspaloy and to stresses which exceed the shear strength of gold. The sources of stress are centrifugal force on the gold plating and thermal stresses due to differences in thermal expansion between gold and Waspaloy.

It was the purpose of the present study to investigate the uptake and elimination of both high pressure hydrogen (5,000 psi) and electrolytically formed hydrogen by bare and gold-plated Waspaloy at room temperature (24°C).

THEORETICAL METHODS FOR THE ELECTROCHEMICAL DETERMINATIONS OF HYDROGEN CONCENTRATIONS IN METALS

The Zakroczymski Method

A new method has been proposed by Tadeusz Zakroczymski [2] for the electrochemical determinations of hydrogen concentrations in metals. This method will be referred to as the "new method." It has the advantage that specimens of various shape and size can be used, not just thin membranes, and that not only diffusible hydrogen can be determined but also hydrogen related to diverse traps and unstable hydride phases. Although the method has been derived for both flat plate and cylindrical specimens, only the flat plate type will be considered here, since all measurements in this study were made with specimens of that geometry.

The following conditions should be satisfied: the flat plate thickness is small compared with its remaining dimensions, and the initial concentration C_0 throughout

the specimen is constant. Although the conditions call for a thin specimen, the sample must be thick enough so that the following condition is satisfied [3]:

$$t_m = \frac{L^2}{4D} \quad (1)$$

Here, L is the thickness of the sample and D is the diffusion coefficient of hydrogen in the metal. When this condition is satisfied, 93.1 percent of the hydrogen will have diffused out of the sample after a time t_m . For Waspaloy metal ($D = 2.7 \times 10^{-8} \text{ cm}^2/\text{sec}$), a thickness of 0.159 cm (1/16 in.) gives a maximum measurement time of 234,000 sec.

For a flat plate, the amount of hydrogen desorbed, Q_H , at time t is given by the following equation [4]:

$$Q_H = Q_H^\infty \left\{ 1 - \frac{8}{\pi^2} \left[\exp(-t/\tau) + \frac{1}{9} \exp(-9t/\tau) + \frac{1}{25} \exp(-25t/\tau) + \dots \right] \right\} \quad (2)$$

Here, $\tau = L^2/\pi^2 D$. It is assumed that a blank has been run on the sample and the values of the blank subtracted from those of the hydrogen containing sample in the above equation.

The hydrogen desorption rate, I_H , at moment t , the quantity measured directly in this method, can be expressed as:

$$I_H = \frac{dQ_H}{dt} = \frac{8 Q_H^\infty}{\pi^2 \tau} \left[\exp(-t/\tau) + \exp(-9t/\tau) + \exp(-25t/\tau) + \dots \right] \quad (3)$$

After a sufficiently long time, the first terms of equations (2) and (3) afford a good approximation:

$$Q_H = Q_H^\infty \left[1 - \frac{8}{\pi^2} \exp(-t/\tau) \right] \quad (4)$$

$$I_H = \frac{8 Q_H^\infty}{\pi^2 \tau} \exp(-t/\tau) \quad (5)$$

Equation (4) is important in that it provides a means for calculating the effect of cut-off of data measurement after a finite time t . Then:

$$Q_{HM}^{\infty} - Q_{HM} = Q_H^{\infty} - Q_H \quad (6)$$

where Q_{HM} is the total quantity of electricity measured in the experiment. Once Q_H^{∞} and τ have been determined, Q_H is determined using equation (4) and a correction is applied to Q_{HM} using equation (6) to obtain Q_{HM}^{∞} . Q_{HM} is obtained by integration of the time-current curve. This was accomplished by numerical integration of the curves with a PDP-11/45 computer using the trapezoidal rule. A similar treatment was carried out for the blank run and Q_B subtracted from the value of Q , obtained by integrating the curve for the hydrogen containing sample, to obtain Q_{HM} .

By taking logarithms of equation (5) one obtains

$$\log I_H = \log \alpha + \beta t \quad (7)$$

where:

$$\alpha = \frac{8 Q_H^{\infty}}{\pi^2 \tau} \quad (8)$$

$$\beta = \frac{-\log e}{\tau} = -\frac{1}{2.303\tau} \quad (9)$$

Thus, after a certain time, the logarithm of the desorption rate is a linear function. From the slope, the diffusion coefficient may be found:

$$D = -0.233L^2\beta \quad (10)$$

and subsequently:

$$Q_H^{\infty} = -0.536 \alpha/\beta \quad (11)$$

Once Q_H^{∞} and Q_H have been determined, Q_{HM}^{∞} , the quantity of interest, can be calculated [equation (6)]. Then the total initial hydrogen concentration C_0 is given by:

$$LC_0 = Q_{HM}^{\infty} \quad (12)$$

and the diffusible (interstitial) hydrogen by:

$$LC_0 = Q_H^{\infty} \quad (13)$$

A plot of $\log I_H$ versus time is shown in Figure 1 for a Waspaloy sample exposed to high pressure hydrogen (5,000 psi) for 1 hr. The curve becomes linear after about 60,000 sec. Points from 80,000 sec to 200,000 sec were fitted using the method of least squares to obtain the parameters α and β . Hydrogen absorbed at high pressures is essentially all contained in the interstitial solid solution of the metal, as will be described later, and the curve I_H versus time should follow equation (3) rather closely. Such a plot is shown in Figure 2 for both the observed and theoretical curves. The theoretical curve was calculated using equation (3), with 17 terms being used in the calculation, and the parameters Q_H^∞ and τ obtained from the least squares fit of equation (7) at large time. The calculation was performed by computer using a program developed by Busing and Levy [5]. Agreement of the observed and theoretical curves is satisfactory, and indicates that the sample geometry (radius 0.64 cm and thickness 0.198 cm) is not too far out of line.

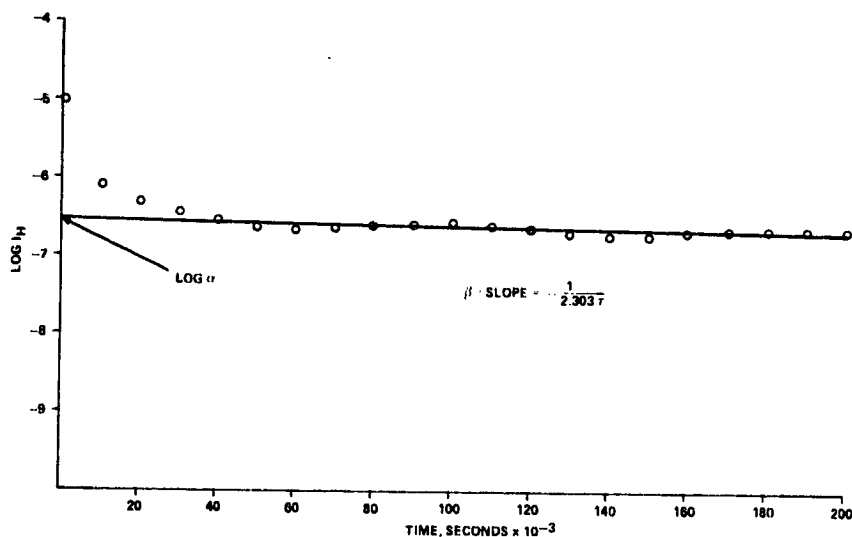


Figure 1. Plot of $\log I_H$ versus time for the new method.

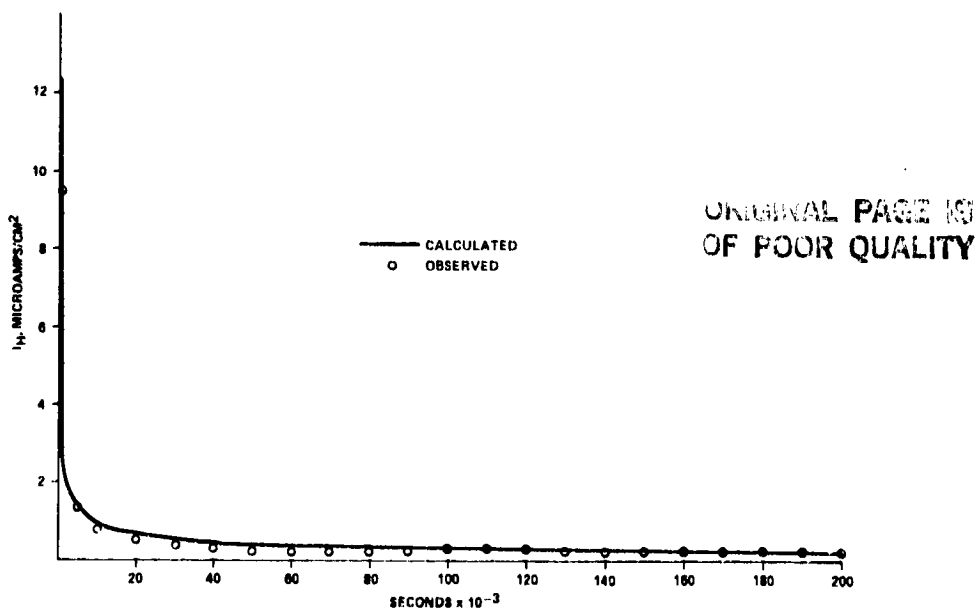


Figure 2. Plots of observed and theoretical curves for I_H versus time in the new method.

This method is therefore an absolute method which provides for determination of the diffusion coefficient, as well as the absolute value of the hydrogen concentration. Furthermore, it provides a means for determining "fast" hydrogen, that is, hydrogen which is evolved faster than the diffusion process would allow. Such hydrogen is attributed to surface and subsurface hydride phases which are unstable at room temperature [2]. The diffusible hydrogen is given by Q_H^∞ . If Q_{HM}^∞ is greater than Q_H^∞ , part of the hydrogen contained in the sample is of the so-called "fast" type, while, if $Q_{HM}^\infty = Q_H^\infty$, all of the hydrogen is contained in the interstitial solid solution of the metal and is controlled by the diffusion process. A disadvantage of this method is that it requires a long period of time for collecting experimental data. In this study a maximum time of 200,000 sec, or approximately 56 hr, was used for collecting the data. The same period of time was also required for running the sample blanks. Another disadvantage is that some of the hydrogen trapped in blisters may remain undesorbed because of a relatively low room temperature. Therefore, in these particular cases, to determine the entire hydrogen other methods based on extraction at an elevated temperature should be used. The electrochemical method has the advantage in that it can detect small quantities of hydrogen and determine their concentration rather accurately, whereas extraction methods are not capable of doing this. For example, the accuracy of determination for a sample containing 1.7 ppm of hydrogen is ± 0.4 ppm using fusion techniques. In this study, the error associated with each determination with electrochemical techniques is estimated at about 8 percent of the value obtained.

The Cottrell Equation

This method [6], unlike the "new method" described in the preceding section, is not an absolute method for the determination of the hydrogen concentration C_0 in that an a priori knowledge of the value of the hydrogen diffusion coefficient is required. Also, it does not distinguish between "fast" hydrogen and hydrogen controlled by the diffusion process but, rather, assumes that all hydrogen is diffusion controlled. However, hydrogen concentrations, at least on a relative basis, can be determined in as little as 30 min if the value of D is known. If the hydrogen is entirely diffusion controlled, as in the case where it is entirely in the interstitial solid solution of the metal, this method provides an accurate and rapid means for determining hydrogen concentrations in metals. In cases where the hydrogen consists of surface and subsurface hydrides, which represent the "fast" hydrogen, the hydrogen is released faster than can be accounted for by the diffusion process and leads to high results for hydrogen concentrations. However, the method can be used to determine hydrogen concentrations on a relative basis in this case. Basic considerations for this method involve the assumption that semi-infinite diffusion occurs in a sample of finite thickness. The solution of the diffusion equations:

$$I = -ZFD \left(\frac{\delta C}{\delta X} \right)_{X=0} \quad (14)$$

$$\frac{\delta^2 C}{\delta X^2} - \frac{1}{D} \left(\frac{\delta C}{\delta t} \right) = 0 \quad (15)$$

leads to the well known Cottrell equation for the permeation current I_p :

$$I_p = ZFC_0 \left(\frac{D}{\pi t} \right)^{1/2} \quad (16)$$

Here, Z is the number of electrons involved in the reaction (one in the case of hydrogen), F is the Faraday constant, D is the diffusivity of the hydrogen through the metal, and I_p is the current density at time t . It is assumed that a blank has been previously run on the sample and its values subtracted from those of the hydrogen containing sample to obtain the current due to hydrogen, I_p . As in the case of the "new method," equation (16) holds for a period of time given by equation (1). The hydrogen concentration can be determined from a plot of I_p versus $\log t$ in the form:

$$\log I_p = \log \frac{ZFD^{1/2}}{\pi^{1/2}} C_0 - 1/2 \log t \quad (17)$$

The plot is a straight line with slope $-1/2$. For Waspaloy metal, for which $D = 2.7 \times 10^{-8} \text{ cm}^2/\text{sec}$, as determined in this work, equation (17) reduces to:

$$\log C_0 = \log I_p + 1/2 \log t - 1.86199 \quad (18)$$

Here, t is the time in seconds, I_p is the diffusion current density in $\mu\text{A}/\text{cm}^2$, and C_0 is the hydrogen concentration in parts per million (ppm). It is standard practice to measure the current after a longer time period, e.g. 30 min, in order to calculate the hydrogen concentration since there is less contribution from the passivation process (and any other oxidation process) at this point.

An alternate procedure for the determination of C_0 , and the one which was finally adopted in this study, is based on integration of the current-time curve of some selected time interval between t_1 and t_2 to give a charge Q_H according to:

$$C_0 = \frac{\pi^{1/2} Q_H}{2ZFD^{1/2} (t_2^{1/2} - t_1^{1/2})} \quad (19)$$

For Waspaloy metal, with the integration performed between 60 and 1800 sec, the equation becomes:

$$C_0 = 199.71 Q_H \quad (20)$$

Integrations to obtain values of Q were performed by numerical integration of the time-current curve with a PDP-11/45 computer using the trapezoidal rule. Values of Q for the blank determinations were obtained in the same way as those for the hydrogen containing samples, and the total electricity due to hydrogen only was obtained by subtraction:

$$Q_H = Q_T - Q_B \quad (21)$$

where Q_H is the number of coulombs due to hydrogen, Q_T is the number of coulombs due to the hydrogen-containing sample, and Q_B is the number of coulombs due to the sample blank. This method produced the most accurate and reproducible results, since it involves the complete time-current curve and not just its value at a single point, as in the case of equation (18). Where hydrogen concentrations are very small it is advisable to plot I_p versus $\log t$ to assure that the function is a straight line with slope close to a value of $-1/2$.

Finally, the electrochemical method provides a useful means for determining hydrogen concentrations in metals with diffusion coefficients larger than 10^{-19} or 10^{-11} cm^2/sec . Fortunately, most metals of interest satisfy this condition. Unless the hydrogen concentrations are very high, it would not be useful for a metal like titanium, where the diffusion coefficient is 4.0×10^{-16} cm^2/sec [7]. At ordinary hydrogen concentrations, the observed current due to hydrogen diffusion would be quite small, making distinctions between the passivation current and current due to hydrogen extremely difficult.

EXPERIMENTAL

As discussed in the previous section, two separate methods, namely the "new method" and the Cottrell method, were used to interpret the data.

The EG&G-PARC Model 350A corrosion measurement console was employed for all measurements in this work. This instrument contains provision for storing 2000 data points in its memory. At the end of the data collection period, the data were read out to a PDP-11/45 computer for analysis.

The sample holder employed in this study is shown in Figure 3. It presents a sample area of 1.0 cm^2 in contact with the solution in the electrolytic cell, an assembled view of which is shown in Figure 4. The sample holder is shown in the center of the cell, with graphite counter electrodes at the sides and the reference electrode (saturated calomel) at the front.

Samples of Waspaloy metal from two different sources were used in this study. For most of the work, samples approximately 0.198 cm thick were cut from a 1.27 cm (1/2 in.) diameter Waspaloy bolt on hand in the laboratory. For the remaining work, samples machined from a used turbine disk from the Space Shuttle Main Engine, S/N 2279525, were used. Analysis of both samples by X-ray fluorescence spectroscopy was carried out and the results are shown in Table 1. As shown by the analytical

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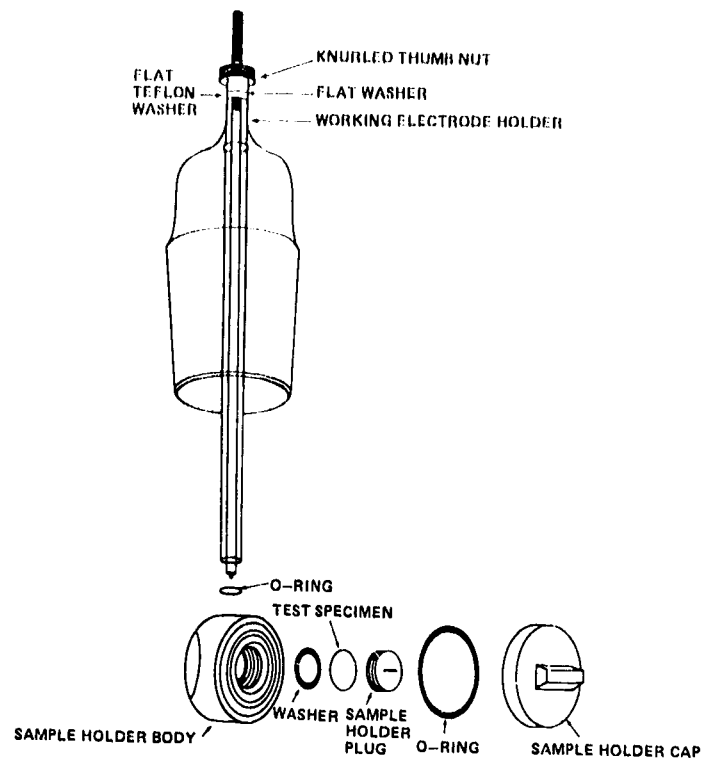


Figure 3. Exploded view of the sample holder.

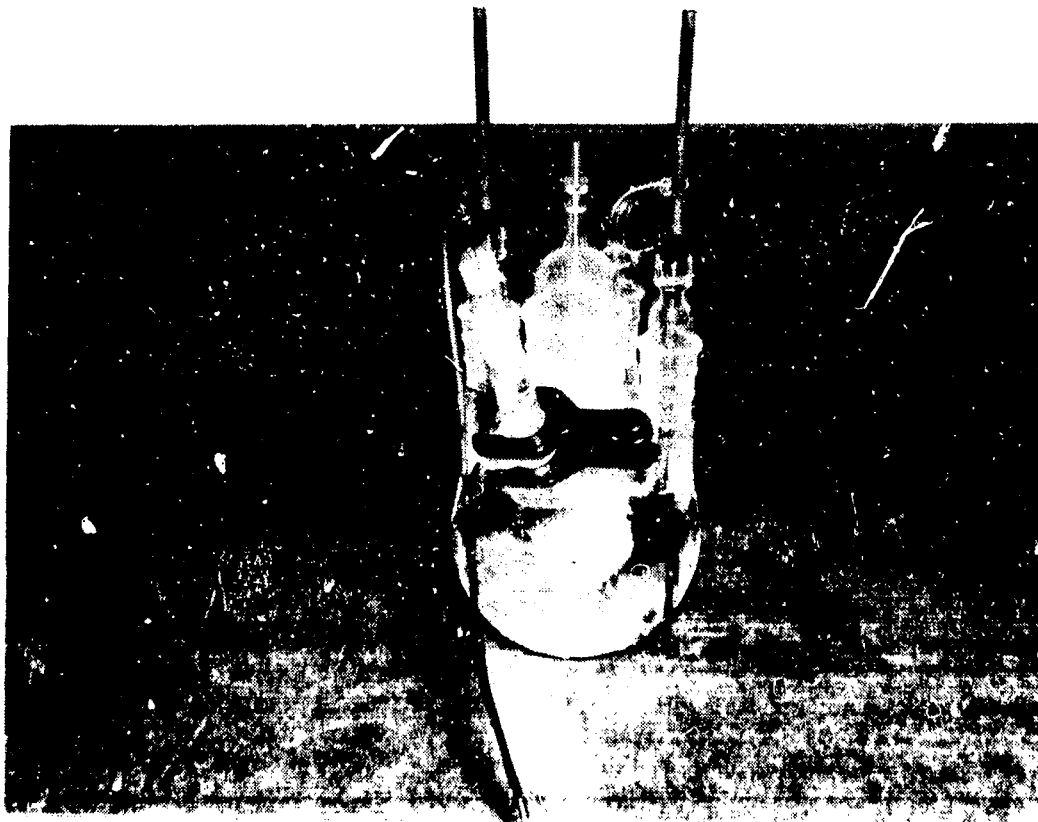


Figure 4. View of the assembled corrosion cell system.

TABLE 1. ANALYTICAL RESULTS FOR WASPALOY METAL FROM BOLT AND TURBINE DISK IN UNITS OF WEIGHT PERCENT

Sample Source	Cr	Co	Mo	Ti	Fe	Al	Si	Mn	Cu	Ni
Waspaloy Bolt	18.82	13.34	4.33	2.94	0.11	1.29	0.69	0.17	0.03	58.28
Turbine Disk	19.11	13.83	3.93	3.08	0.08	1.35	0.72	0.18	0.04	57.68

results, both metals are quite similar in composition, and differ only in method of preparation (heat treatment, etc.). The surfaces of the metal were prepared by wet sanding with 150C and 220A grit silicon carbide paper and finally polishing on 4/0 grit polishing paper. They were then de-greased in boiling trichloroethylene, and sample blanks were run at a constant potential of +0.25 V (NHE) in a solution of 0.1N NaOH at room temperature (24°C). For the "new method," blanks were taken for a period of 200,000 sec at 500 sec intervals, while they were taken for a total of 1800 sec at 60 sec intervals for the Cottrell method. Data for hydrogen containing samples were collected under the same conditions.

In cases where it was necessary to charge the samples with hydrogen, the charging was carried out in two ways. For charging with high pressure hydrogen, the samples were exposed to a hydrogen atmosphere of 5,000 psi at ambient temperature for various lengths of time. For charging with electrolytically formed hydrogen, all samples were charged in 0.1N H₂SO₄ at a current density of 60 mA/cm² for 1 hr.

Gold Plating and Electropolishing

Gold plated Waspaloy samples, with plating thicknesses of 0.0127 mm (0.0005 in.), 0.0254 mm (0.001 in.) and 0.061 mm (0.0024 in.), for investigating the take-up of high pressure hydrogen at room temperature were electroplated according to the procedure given in Table 2. The procedure for electropolishing Waspaloy metal is given in Table 3.

RESULTS AND DISCUSSION

Hydrogen Uptake by Bare Waspaloy Metal at 24°C

Hydrogen uptake by bare Waspaloy metal was investigated at room temperature for both samples charged with high pressure hydrogen (5,000 psi) and for electrolytically charged samples. For the high pressure charging, exposure times of 0.5, 1 and 3 hr were used employing a 0.198 cm thick sample cut from a 1.27 cm (1/2 in.) diameter Waspaloy bolt. The same sample was used for all three determinations, the remaining hydrogen being removed from the sample by baking at 191°C (375°F) for 3 hr after each determination. It was established that the hydrogen was completely removed by the running of blanks after the baking process. A word of caution is in order in that the baking time necessary for the complete removal of hydrogen depends on the thickness of the sample. For a flat plate of thickness L, equation (1) gives the following relation:

TABLE 2. PROCEDURE FOR GOLD ELECTROPLATING OF WASPALOY

1. Solvent wipe to remove grease, oil, etc.
2. Make the part the anode for 1/2 to 2 min in a commercial alkaline cleaner operated at a temperature of approximately 66°C and a current density of 21.5 mA/cm².
3. Rinse in flowing water.
4. Acid pickle for 1 to 1.5 min in a bath containing 150 ml of nitric acid (70%), 240 ml of phosphoric acid (75%), 70 ml of glacial acetic acid, 240 ml of hydrochloric acid (37%), and 70 ml of deionized water operated at a temperature of 51.7°C to 79.4°C.
5. Rinse in flowing water.
6. Cathodic activate for 1 to 2 min in a 38 to 44% by weight sulfuric acid bath operated at room temperature.
7. Rinse in flowing water.
8. Nickel strike for 3 to 5 min at a current density around 43 mA/cm² in a bath containing 224.7 to 239.7 gm/l of nickel chloride, 89.9 to 93.6 gm/l of hydrochloric acid (37%), and deionized water (operated at room temperature).
9. Rinse in flowing water.
10. Gold strike for 10 to 15 sec in a commercial (Aurobond) acid bath containing 0.75 to 1.87 gm/l of gold and operated at 37.8°C.
11. Rinse in flowing water.
12. Gold plate to required thickness at a current density of 10.8 mA/cm² in a commercial acid bath (Autronex Process) containing 7.0 gm/l of gold and operate at around 37 8°C.

TABLE 3. PROCEDURE FOR ELECTROPOLISHING OF WASPALOY

1. Solvent wipe to remove grease, oil, etc.
2. Clean by soaking for 15 to 20 min in a commercial alkaline cleaner operated at a temperature of approximately 65.6°C.
3. Rinse in flowing water.
4. Electropolish by making the part the anode for approximately 3 min in a commercial electropolishing solution ("Technical Micronics Control", Type I) at a current density of 0.807 A/cm².

$$\frac{t(L)}{t(0.198 \text{ cm})} = \frac{L^2}{0.198^2} \quad (22)$$

Thus, if 0.198 cm thick sample requires 3 hr for baking, a flat sample 2.54 cm thick would require 494 hr or about 21 days. However, the hydrogen in the 0.198 cm thick sample is probably completely removed in a much shorter time than the 3 hr baking time employed in this study. Results for the hydrogen concentrations found for each exposure time, employing both the "new method" and the Cottrell method, are listed in Table 4. The value of the hydrogen diffusion coefficient, obtained using the "new method," used in the Cottrell equation was the mean of the five determinations listed in Table 5, namely, $2.7 \times 10^{-8} \text{ cm}^2/\text{sec}$. The standard error obtained in these five determinations is $\pm 0.8 \times 10^{-8} \text{ cm}^2/\text{sec}$. As seen from Table 5, the values of D are significantly higher for the electrolytically charged samples. The value of D for the sample cut from a used turbine disk is about the same as that for a sample cut from the Waspaloy bolt, as determined by electrolytic charging.

TABLE 4. ANALYTICAL RESULTS OBTAINED FOR HYDROGEN CONCENTRATIONS IN BARE WASPALOY AT 24°C

Sample Source	Method of Charge	Time of Charge	C_o (ppm) NM**	C_o (ppm) Cottrell Method	Percent Interstitial H ₂
Waspaloy Bolt	High Pressure*	1/2 hr	0.23	0.32	100
Waspaloy Bolt	High Pressure	1 hr	1.1	1.6	100
Waspaloy Bolt	High Pressure	3 hr	0.40	1.4	75
Waspaloy	Electrolysis	1 hr	0.60	2.7	20
Turbine Disk ¹	Electrolysis	1 hr	0.67	2.9	30
Turbine Disk	High Pressure	1 hr	—	1.0	—

* All high pressure charges were made at 5,000 psi.

** "New Method"

1. Sample was machined from part S/N 2279525.

TABLE 5. VALUES OF THE DIFFUSION COEFFICIENTS OBTAINED BY THE NEW METHOD FOR WASPALOY METAL AT 24°C

Sample Source	Method of Charge	Time of Charge	$D \times 10^8$ (cm ² /sec)
Waspaloy Bolt	High Pressure	0.5 hr	1.0
Waspaloy Bolt	High Pressure	1 hr	0.8
Waspaloy Bolt	High Pressure	3 hr	2.8
Waspaloy Bolt	Electrolysis	1 hr	4.8
Turbine Disk*	Electrolysis	1 hr	4.3

* Sample machined from part number S/N 2279525.

As shown by the concentrations listed in Table 4, results are in fairly good agreement for the Cottrell method and the "new method" at exposure times of 0.5 and 1 hr. For the 3 hr exposure time the result using the "new method" is quite a bit lower than expected, and is lower than the result obtained for a 1 hr exposure. This may be attributed to a change in the sample surface conditions, probably caused by polishing the sample surface for an extended period of time between exposures. Hydrogen uptake at high pressures was subsequently found to be sensitive to sample surface conditions and led to the discovery of the effect of electropolishing, which will be described later. The result for the 3 hr exposure using the Cottrell method is about the same as that for the 1 hr exposure. These results, in general, indicate that the sample becomes saturated with hydrogen after about 1 hr of exposure. A plot of the values of the hydrogen concentrations, obtained using the Cottrell method, is shown in Figure 5. A "best fit" to these points was obtained using the following relation:

$$C_o = \frac{at^2}{1 + bt^2} \quad (23)$$

Here C_o is the hydrogen concentration in ppm and t is the charging time in minutes, a and b being constants. The points were fitted using a non-linear least squares program developed by Busing and Levy [5], with the values 1.145×10^{-3} and 6.92×10^{-4} being obtained for the parameters a and b , respectively. Thus, for this particular sample, the value a/b , and hence C_o , approaches the limiting value 1.65 ppm

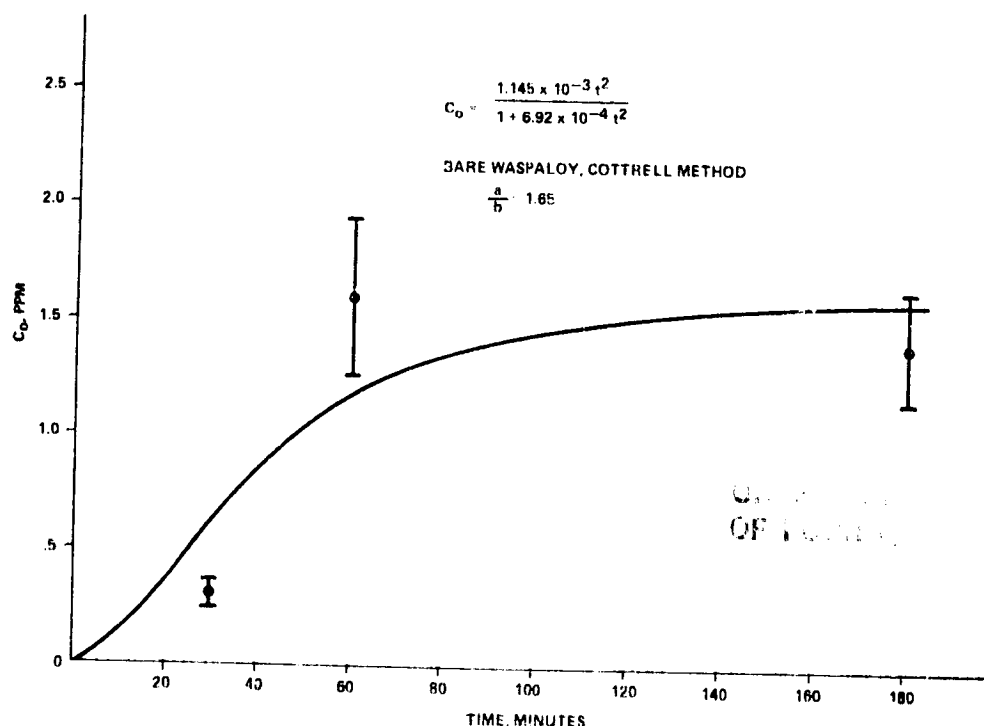


Figure 5. Plot of hydrogen uptake versus time of exposure with fit by a theoretical curve.

at large time. Further evidence that the interior of the sample has become saturated with hydrogen after a 3 hr exposure is given by the percent interstitial hydrogen at that point (75 percent). Thus, only 75 percent of the hydrogen is contained in the interstitial solid solution of the metal, the remainder being surface hydrogen, as obtained using the "new method." For the 0.5 and 1 hr exposures, 100 percent of the hydrogen is contained interstitially. The result for the saturation value (1.7 ppm) at room temperature is quite a bit less than the 25 ppm observed in a used turbine disk which had been exposed to high pressure hydrogen at high temperature (1200°F). The ability of the Waspaloy metal to absorb much higher concentrations at high temperature can be attributed to the following factors. First, at high gas pressures, the rate of diffusion is proportional to the square root of the pressure, suggesting that the dissolved gas is in the form of atoms rather than of molecules [8]. At high temperature, the hydrogen gas will be more highly dissociated, making more atomic hydrogen available for diffusion. Second, the diffusion coefficient for the hydrogen in the Waspaloy metal will be much larger at high temperature and diffusion of the hydrogen will become much more rapid. Third, thermal expansion of the crystal lattice of the metal creates more space for hydrogen atoms to occupy interstitial positions in the lattice. Also high stresses, as encountered by the turbine disk during engine operation, increase the solubility of hydrogen in the metal.

For the electrolytic charging, samples were charged for a 1 hr period in 0.1N H_2SO_4 at a current density of 60 mA/cm². Samples charged electrolytically were much less sensitive to sample surface conditions than those charged at high pressure. The results for hydrogen concentrations obtained in this way are also listed in Table 4 for both the Cottrell method and the "new method." In contrast to the results obtained for high pressure charging, 70 to 80 percent of the hydrogen is in the form of surface hydrogen. This is believed to consist of surface and subsurface hydrides which are unstable at room temperature [2]. As stated previously, the Cottrell method leads to high results for the hydrogen concentrations in such cases. This is shown in Table 4, where the hydrogen concentrations are much higher for the Cottrell method than for the "new method." This is because, in the early stages where the Cottrell method is used, loss of hydrogen is occurring much more rapidly than the diffusion process would allow. However, the values of the diffusion coefficient obtained by electrolytic charging are correct, since they are obtained from measurement of the current at large times. Results are listed in Table 4 for a sample cut from the Waspaloy bolt and a sample machined from a used turbine disk, S/N 2279525. The results, obtained from electrolytic charging of both samples under the same conditions, are in excellent agreement, showing that the hydrogen uptake behavior of both samples is similar. Also shown is a result from high pressure charging of a sample from the material in the used turbine disk as obtained using the Cottrell method. Although, as stated previously, the uptake of hydrogen is sensitive to sample surface conditions, the agreement between that for the turbine disk (1.0 ppm) and that for the Waspaloy bolt (1.6 ppm) is quite good.

Analysis of Samples Taken from a Used Turbine Disk

Two samples, 1.43 cm diameter and 0.16 cm thick, were machined from a used turbine disk (S/N 2279525). The samples were analyzed for hydrogen content immediately after machining using the Cottrell method. Data for the hydrogen containing sample were collected first. The samples were then baked for 3 hr at 191°C (375°F) to remove the remaining hydrogen and blanks were subsequently run. Hydrogen concentrations of 0.36 and 0.40 ppm were obtained. The average value, 0.38 ppm, is

quite significant considering the length of time which elapsed between the time the sample was cut from the disk and the time of analysis. As will be discussed later, the gold plate on the turbine disk seals in the hydrogen and prevents it from diffusing out of the sample until the part is cut. After cutting, hydrogen diffuses out of the metal rather rapidly, reducing hydrogen concentrations to rather small values. A more complete description of the hydrogen elimination process will be given in the following section. The rather high value of the hydrogen concentration thus suggests that the initial hydrogen concentration was quite large. This is consistent with determinations by Rocketdyne, in which concentrations as high as 25 ppm were observed. These results also verify the results of the preceding section in that the hydrogen is certainly contained in the interstitial solid solution of the metal as a result of high pressure charging.

Hydrogen Elimination by Bare Waspaloy

Studies of hydrogen elimination were made using the Cottrell method. Samples were charged with hydrogen both at high pressure (5,000 psi) and by electrolytic means. From the results of the first part of this section concerning hydrogen uptake, it is evident that the rate of elimination for samples charged at high pressure should be different from that for samples charged electrolytically. As stated previously, the samples charged at high pressure contain hydrogen in the interstitial solid solution of the metal, while the electrolytically charged samples consist mostly of surface hydrogen. Thus, the rate of elimination should be slower for the samples charged at high pressure and, possibly, the kinetic mechanisms can be different.

It has been shown previously by one of the authors [9] that hydrogen elimination by electrolytically charged samples follows rather closely a first order rate law. That is, the rate of elimination is proportional to the concentration:

$$\frac{-dC}{dt} = kC \quad . \quad (24)$$

Here, C is the hydrogen concentration at time t . Upon integration and imposition of proper boundary conditions, equation (24) becomes:

$$\ln \frac{C}{C_0} = kt \quad . \quad (25)$$

Here, C is the hydrogen concentration at time t and C_0 is the initial hydrogen concentration. The corresponding half life for hydrogen elimination is given by:

$$t_{1/2} = \frac{-1}{k} \ln 0.5 = \frac{0.693}{k} \quad . \quad (26)$$

A plot of $\ln C/C_0$ versus time at 24°C is shown in Figure 6 for both electrolytically charged and high pressure charged samples. As seen from the plots, the values for the rate constant are quite different for the two cases. For the electrolytically

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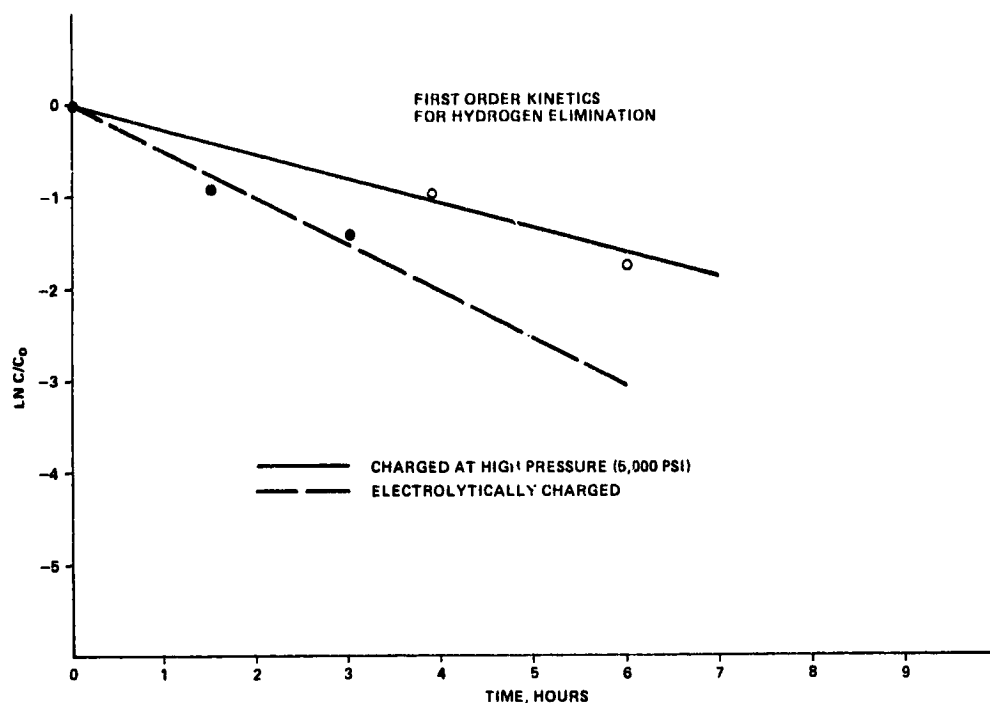


Figure 6. Plot of $\ln C/C_0$ versus time for both electrolytically charged and high pressure charged samples following first order kinetics.

charged sample, a value of $k = 0.52 \text{ hr}^{-1}$ was obtained with a corresponding half life of 1.3 hr, while a value $k = 0.25 \text{ hr}^{-1}$ with a half life of 2.8 hr was obtained for the sample charged at high pressure. However, as shown in Figure 7, the results for hydrogen elimination for a sample charged at high pressure also follow very closely a curve corresponding to zero order kinetics. That is:

$$-\frac{dC}{dt} = k \quad (27)$$

which becomes on integration:

$$C_0 - C = kt \quad (28)$$

The half life here is given by:

$$t_{1/2} = \frac{0.5 C_0}{k} \quad (29)$$

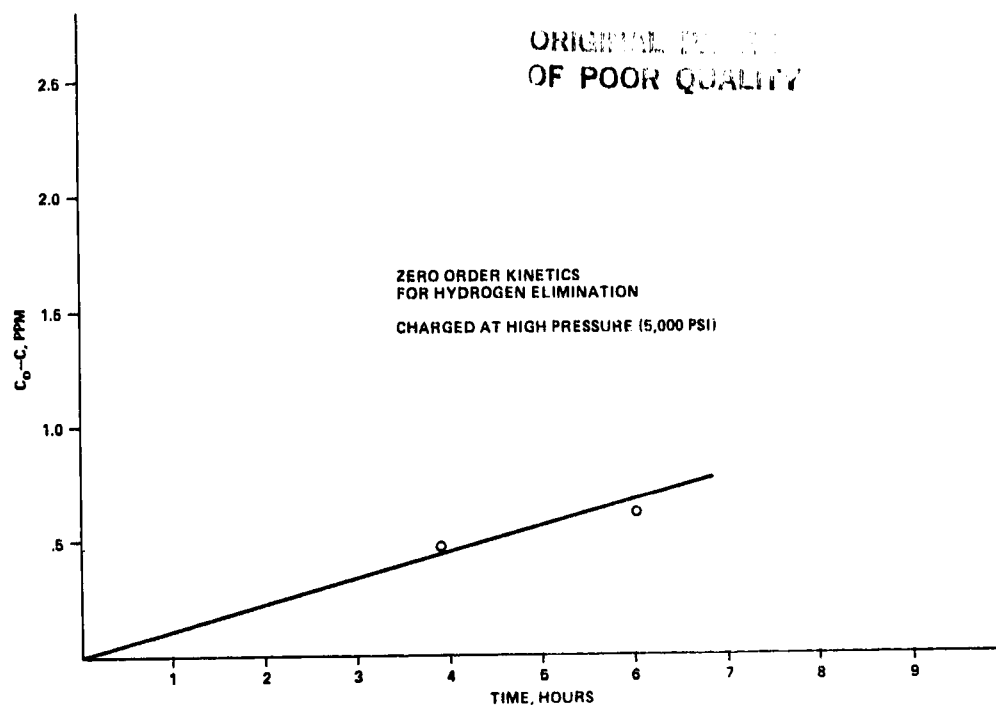


Figure 7. Plot of Co-C versus time for a sample charged with high pressure hydrogen following zero order kinetics.

A value of k equal to 0.112 ppm/hr, with a corresponding half life of 3.4 hr was obtained for this case. The kinetic mechanism for the electrolytically charged samples can be explained rather simply by a metallic hydride decomposing according to the following process:



Reaction (31) should occur rapidly through three body collisions at the sample surface, so that the rate controlling reaction is given by equation (30). Therefore:

$$\frac{-dC}{dt} = kC \quad (32)$$

where $C = [\text{MH}]$, thus giving rise to the first order rate equation. It is attractive to think of the rate of elimination for samples charged with high pressure hydrogen in terms of a zero order process, where diffusion of the hydrogen, rather than decomposition of the metallic hydrides is the rate-determining step. However, as mentioned previously, the hydrogen elimination for samples charged at high pressure also follow rather well the first order rate law, and a definite distinction cannot be made between the two cases.

The rate constants k obtained with this procedure are functions of the sample thickness. To show this, a zero order dependence will be assumed, although the first order dependence leads to exactly the same relation. From equation (1):

$$t_m = \frac{L^2}{4D}$$

For a zero order dependence, when all of the hydrogen has diffused from the sample:

$$C_o = kt_m \quad (33)$$

Equating the two expressions for t_m :

$$\frac{C_o}{k} = \frac{L^2}{4D} \quad (34)$$

and, since all samples in the present study were 0.198 cm thick:

$$k(L) = k (0.198 \text{ cm}) \times \frac{0.198^2}{L^2} \quad (35)$$

where L is the thickness of the sample.

The temperature dependence for the rate of elimination may be obtained by assuming that the Arrhenius equation holds, although it normally applies to reaction rates in solution. The equation is:

$$\log k = A + \frac{B}{T} \quad (36)$$

where T is the absolute temperature. A value of the rate constant for elimination of electrolytically formed hydrogen was obtained at 66°C (150°F). The rate was too fast to measure at 191°C (375°F). Using this value together with the value obtained at 24°C, the following relation was obtained:

$$\log k = \frac{2292.3}{T} + 9.29466 \quad (37)$$

Values obtained experimentally for the elimination of electrolytically formed hydrogen for 0.198 cm thick samples at 24°C and 66°C are listed in Table 6, together with calculated values for 191°C and 649°C. Similar calculations were made for flat plates 2.54 cm (1 in.) thick using equation (35). Thus, these results, while obtained by

TABLE 6. RATE CONSTANTS AND HALF LIVES FOR ELIMINATION OF ELECTROLYTICALLY FORMED HYDROGEN

		L = 0.198 cm		L = 2.54 cm	
T (°F)	T (°C)	k (hr ⁻¹)	t _{1/2}	k (hr ⁻¹)	t _{1/2}
75	24	0.52	1.3 hr	3.2 x 10 ⁻³	9.1 days
150	66	4.7	8.8 min	1.9 x 10 ⁻²	24 hr
375	191	2.3 x 10 ⁴	0.11 sec	1.4 x 10 ²	18 sec
1200	649	6.4 x 10 ⁶	3888 μsec	3.9 x 10 ⁴	0.06 sec

assuming the Arrhenius relation, indicate that hydrogen is eliminated quite rapidly at high temperatures. This is providing that such elimination is not hindered by the presence of gold plating, the effect of which will be described in the next section.

High Pressure Hydrogen Uptake and Elimination by Gold Plated Waspaloy

The Cottrell method was employed for this study, with samples gold plated to thicknesses of 0.0127 mm (0.0005 in.), 0.0254 mm (0.001 in.), and 0.061 mm (0.0024 in.) being used. Blanks were first run on the samples, after which they were exposed to high pressure hydrogen (5,000 psi) for a period of 1 hr. Subsequent runs were then made on the three samples to determine whether hydrogen was diffusing from any of them. In all three cases the runs made on the samples were essentially identical to the blank runs made before exposure, indicating that no hydrogen was diffusing through the gold plate. The gold plate was then removed from one side of the sample with a plating thickness of 0.0254 mm by sanding. Another run was made, after which the sample was baked for 3 hr at 191°C (375°F) to remove any hydrogen which might have been present. The sample was then re-run to obtain the sample blank. In this case the runs made before and after baking were identical, indicating that no hydrogen was present in the Waspaloy metal beneath the gold plate. The procedure was repeated for the sample with 0.0127 mm gold plate, but in this case hydrogen was detected in the Waspaloy metal, its concentration being 0.22 ppm. The breakthrough thickness for the penetration of hydrogen at 5,000 psi through gold plate thus lies between 0.0127 mm and 0.0254 mm of gold plate. The hydrogen penetrates the gold plate at high pressure, but the gold plate then acts as a trap, preventing the reverse process, diffusion of the hydrogen out of the sample, from occurring. Using the value of 0.0127 mm thickness as the breakthrough point, with an exposure time of 1 hr, an approximate value of the diffusion coefficient for hydrogen at 5,000 psi in gold can be obtained by the following relation:

$$X = (2Dt)^{1/2} \quad (38)$$

Here, X is the depth of sample penetrated in cm and t is the time of exposure in seconds. The value of D thus obtained was 2.24 x 10⁻¹⁰ cm²/sec at 24°C. This is considered a minimal value, since the actual breakthrough point is probably somewhat larger than 0.0127 mm.

The temperature dependence of the diffusion coefficient is given by the following equation [4]:

$$D = D_0 e^{-E/RT} \quad (39)$$

where T is the absolute temperature. A value of E was not available for gold, but the corresponding value of 6800 cal for Pd [4] was used along with the diffusion coefficient for high pressure hydrogen in gold (2.24×10^{-10} cm²/sec at 24°C) to obtain an approximate value of the diffusion coefficient of hydrogen in gold at 5,000 psi and a temperature of 649°C (1200°F), the approximate operational environment of the turbine disk in the Space Shuttle Main Engines. The value of D obtained in this way was 5.52×10^{-7} cm²/sec. Using this value of D and equation (38), the thickness of gold penetrated in 10 min, the approximate operating time of the main engines during launch, is 0.254 mm (0.010 in.). Thus, according to these calculations, it is possible that hydrogen can actually penetrate the gold plate (0.127 mm max.) under the operating conditions of the main engine. However, these calculations are subject to experimental verification.

While these calculations indicate that hydrogen may actually be penetrating the gold plate of the turbine disk, there is no doubt that hydrogen penetration into the Waspaloy metal is slowed down by the gold plate. By the same token, the reverse process, elimination of hydrogen from the Waspaloy metal, is also hindered. Also, after engine shut-off and cool-down of the turbine disk, the gold plate acts as a trap and prevents further diffusion of hydrogen out of the turbine disk. As a result, the hydrogen concentration continues to build up in the turbine disk, and, after several engine starts, may reach a saturation level. At this point hydrogen will accumulate on the metal surface and exist as surface hydrogen just beneath the gold plate. Evidence that such saturation occurs in bare Waspaloy at room temperature, with the formation of surface hydrogen as a consequence, has been obtained in this study, although the level of hydrogen concentration to reach saturation, if it occurs at high temperature will be much longer.

Effect of Electropolishing on High Pressure Hydrogen Uptake at 24°C

An apparent lack of reproducibility in results obtained through high pressure hydrogen charging of samples led to a study of the effect of electropolishing the sample surface. The uptake of hydrogen under high pressure was found to be quite sensitive to sample surface conditions. It has been known for many years [4] that polishing of the sample surface, using the usual techniques, results in a pronounced decrease in the ability of a metal to take up hydrogen at high pressures. A study of the influence of surface treatments and coatings on the embrittlement of high strength steels by hydrogen under pressure revealed that electropolishing was very effective in increasing the hydrogen pressure required to rupture disks of 35 NiCrMo 16 steel [10], and, in fact, was much more effective than shot peening.

The surface of a Waspaloy sample was prepared by sanding with 150C and 220A grit silicon carbide paper and finally polishing with 4/0 grit polishing paper. The sample was then subjected to a high pressure hydrogen environment for 1 hr, after which its hydrogen content was measured as 0.75 ppm. The surface of the sample was then electropolished using the procedure described in Table 3 and the sample

was subjected to high pressure hydrogen charging under the same conditions as before. The resulting hydrogen uptake was only 0.04 ppm. Thus, electropolishing results in a rather drastic decrease in the ability of a metal to absorb hydrogen at high pressure. It may provide a useful alternative to shot-peening, where surface compression is applied to decrease the hydrogen take-up ability of the metal.

CONCLUSIONS

Electrochemical Methods

The "new method" for the analysis of hydrogen concentrations in metals provides a useful way to distinguish between "fast" hydrogen and hydrogen elimination controlled by the diffusion process. In the latter case, the hydrogen is supposedly contained in the interstitial solid solution of the metal, while in the former case the hydrogen is mainly present as surface and subsurface hydrides which are unstable at room temperature [2]. This hydrogen is therefore eliminated faster than could be accounted for by the diffusion process. It is an absolute method in that absolute values of the hydrogen concentrations are determined, as well as the hydrogen diffusion coefficients. Its main drawback is the length of time, e.g. 100 hr, which is required for data collection.

The Cottrell method provides a much faster procedure for the determination of hydrogen concentrations in metals, the total time for a single determination being about 1 hr. It assumes that all hydrogen desorption is controlled by diffusion, and leads to high results where hydrogen is eliminated more rapidly than the diffusion process allows, as in the case of the "fast" hydrogen described in the "new method." Further, it is not an absolute method, in that an a priori knowledge of the value of the diffusion coefficient is required. However, in cases where all of the hydrogen desorption is controlled by diffusion, as in the case where the hydrogen is contained in the interstitial solid solution of the metal, the results are accurate, and agree with those obtained using the "new method." For the case of "fast" hydrogen, the Cottrell method can be used to determine hydrogen concentrations on a relative basis.

The electrochemical method may not be used in cases where some of the hydrogen is trapped in blisters and may remain undesorbed because of a relatively low room temperature. Therefore, in these particular cases, to determine the entire hydrogen, other methods based on extraction at an elevated temperature should be used. However, the electrochemical method is capable of determining very small hydrogen concentrations, which could not be determined accurately using fusion or extraction techniques. Finally, the electrochemical method is not useful in cases where the diffusion coefficient is very small, as in the case of titanium ($D = 4.0 \times 10^{-16} \text{ cm}^2/\text{sec}$), since the current due to hydrogen desorption would be too small to measure.

Application of Results to the Turbine Disk of the Space Shuttle Main Engine

Problems have been encountered with the gold plate presently employed to eliminate hydrogen take-up by the Waspaloy metal of the turbine disk in the Space Shuttle Main Engines. Hydrogen is getting into the Waspaloy metal at appreciable concentrations under the operating conditions of the main engines. This has been

attributed to the loss of gold plate through debonding on the downstream face of the fir tree slot area. However, calculations in this study indicate that hydrogen may actually be penetrating the gold plate itself, but these calculations are subject to experimental verification. The presence of gold plate certainly slows down the elimination process. It acts as a trap when the turbine disk cools down and prevents further elimination of hydrogen.

Other calculations in this study have indicated that hydrogen is eliminated from a metal rapidly at high temperature. However, in practice, the engine is cooled quite rapidly by liquid hydrogen after shut-down and precludes the possibility that hydrogen would be expelled by a hot engine. Calculations carried out during this study have indicated that the hydrogen might be completely expelled from the turbine disk by baking for a period of 0.5 to 1 hr at 649°C (1200°F) provided that elimination is not hindered by gold plate. A separate experimental study by one of the authors [11] has indicated that the hydrogen embrittlement phenomenon is reversible provided the hydrogen is removed from the metal before cracking occurs. That is, the mechanical properties of the metal revert to their status before any hydrogen was absorbed.

Although any process which hinders the take-up of hydrogen also hinders its elimination, another possibility is the use of the electropolishing technique, which was found to be effective in this study. This would provide an alternate method to shot-peening, which is currently under investigation. In any case, continuing the search for a good high temperature alloy which is less subject to hydrogen environment embrittlement than Waspaloy is certainly in order. Needless to say, any procedure suggested by this study is subject to many further studies and tests, possibly as a part of an operating engine with which many starts and stops are made and analyses for hydrogen content of the turbine disks performed.

Future work in the areas not included in the present study, especially uptake of hydrogen by bare and gold plated Waspaloy at high temperature and pressure, will be carried out when the proper facilities become available.

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