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HYDROGEN EMBRITTLEMENT

Electrodeposition and electroless deposition and their associated processing steps including acid pickling and electrocleaning can generate hydrogen which can enter substrates in the atomic form and cause hydrogen embrittlement. This chapter outlines the factors which cause hydrogen embrittlement, its subsequent effects and failure mechanisms, and then elaborates on methods for reducing or eliminating the problem. Since steels are particularly prone to hydrogen embrittlement, emphasis is placed on these alloys. A section on permeation of hydrogen through various protective coatings is included to show the effectiveness of various barrier layers on minimizing hydrogen egress to substrates. Some excellent materials science investigative work showing how electroless copper deposits are embrittled by hydrogen is also presented along with data on hydrogen pick-up as a result of chemical milling of various steel and titanium alloys.

Hydrogen embrittlement is a generic term used to describe a wide variety of fracture phenomena having a common relationship to the presence of hydrogen in the alloy as a solute element or in the atmosphere as a gas (1). Louthan (2) lists the following problems as a result of hydrogen embrittlement and/or hydriding: failures of fuel cladding in nuclear reactors, breakage of aircraft components, leakage from gas filled pressure vessels used by NASA, delayed failure in numerous high strength steels, reductions in mechanical properties of nuclear materials, and blisters or fisheyes in copper, aluminum and steel parts. Steels, particularly those with high strengths of 1240 to 2140 MPa (180,000 to 310,000 psi) are prone to hydrogen embrittlement regardless of temperature (3)(4), (Figure 1). However, hydrogen embrittlement is not specific to just high strength steels.

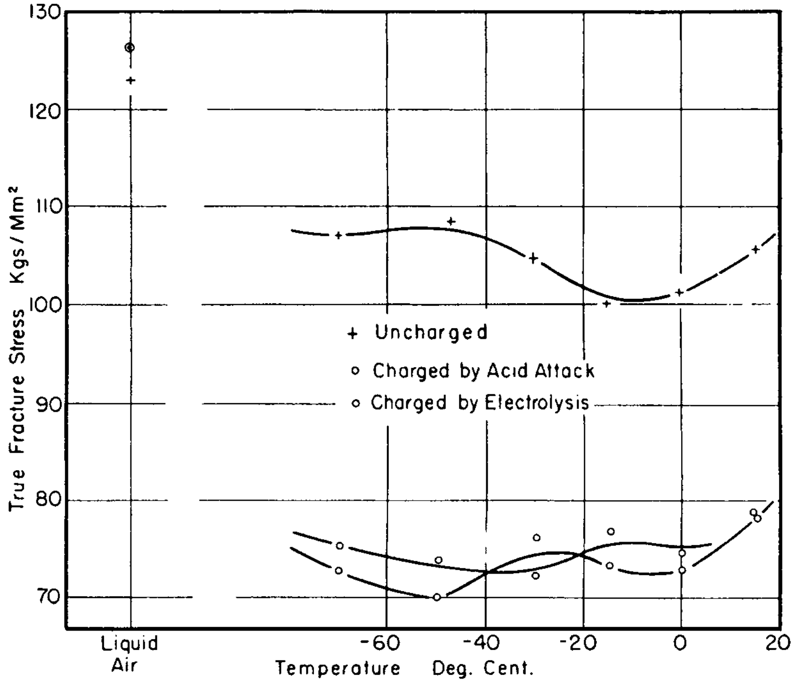

Figure 1: Fracture stress as a function of hydrogen absorption and temperature for 0.08% carbon steel. From reference 4. Reprinted with permission of ASM.

Nickel, titanium, aluminum (4)(5) and even electroless copper deposits (6) exhibit the phenomenon. It appears that any material can become embrittled by a pressure effect if hydrogen bubbles are introduced by a means such as electrodeposition and this state remains unchanged until hydrogen atoms escape from the bubbles (6). In some cases, the failure can be so abrupt and forceful as to seem almost explosive (7). Geduld reminisced that "one of the most spectacular and memorable sounds associated with zinc plating was standing in a quiet storage room next to drums of recently zinc plated steel springs and listening to the metallic shriek of self-destruction. as the springs slowly destroyed themselves in order to release occluded hydrogen" (8).

Some examples of the effects of hydrogen on the structure of metals are shown in Figures 2 through 10. Figure 2 is a photomicrograph of commercial copper that had been heated in hydrogen. The treatment produced a porous, degenerated structure of low strength and ductility. Figure 3 shows the wall of a heavy pressure vessel used in the petrochemical industry that developed large internal blisters and cracks from the action of hydrogen as a result of sulfide corrosion. Figure 4 shows a vanadium wire that literally shattered when it was cathodically charged with hydrogen in an electrolytic cell (9).

Figures 5 through 10 show the influence of hydrogen on steel (10). Figures 5 and 7 are a bar that was not cathodically treated, therefore, was not hydrogen embrittled. The same bar is shown in Figures 6 and 8 after cathodic treatment to introduce hydrogen and the severe damage is clearly evident. Figure 9 is a cathodically treated specimen showing partial relief as a result of heating at 200°C for 5 minutes while Figure 10 shows a sample exhibiting full relief as a result of heating at 200°C for 1 hour.

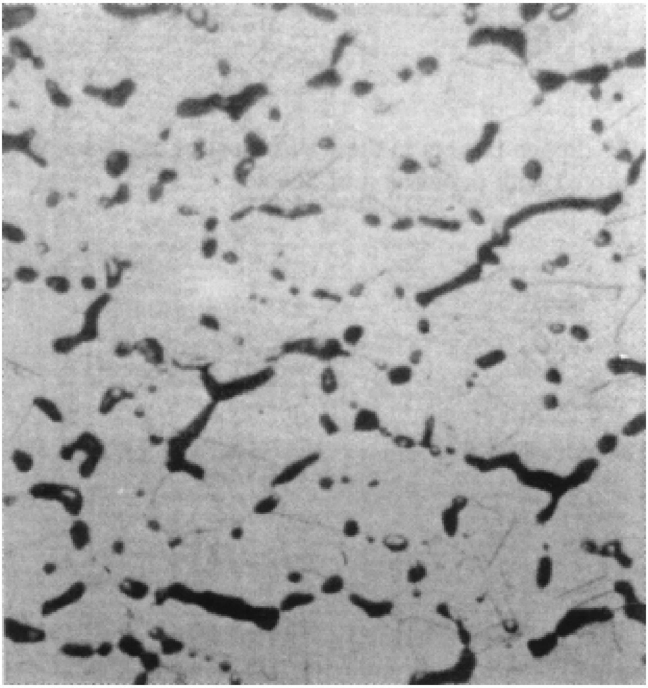

Figure 2: Structure of commercial copper after heating in hydrogen for 3 hours at 750°C (about 250 X). From reference 9. Reprinted with permission of Science.

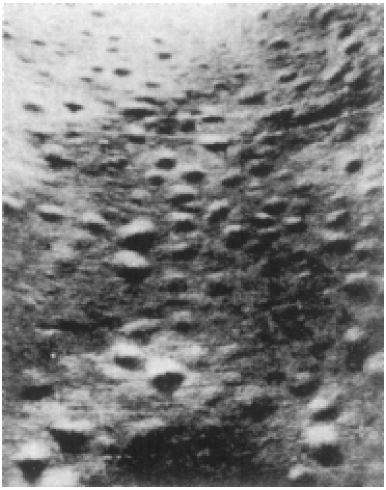

Figure 3: Hydrogen blisters in the wall of a steel container. From reference 9. Reprinted with permission of Science.

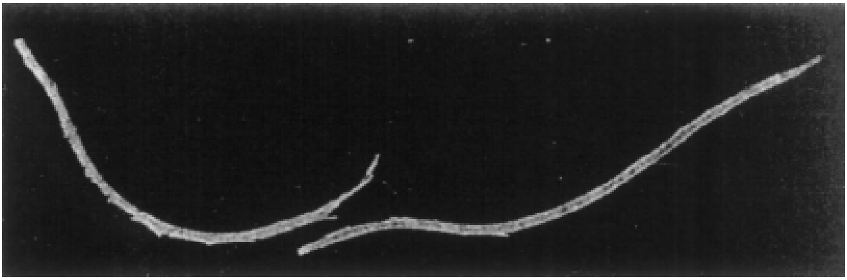

Figure 4: Vanadium wire shattered by cathodic charging with hydrogen. From reference 9. Reprinted with permission of Science.

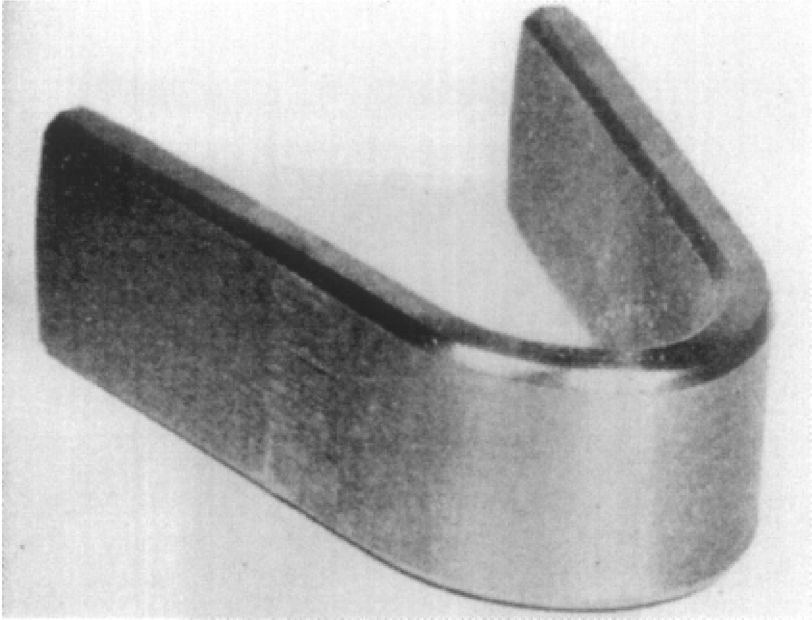

Figure 5: Steel sample with no cathodic treatment (× 1). From reference 10.

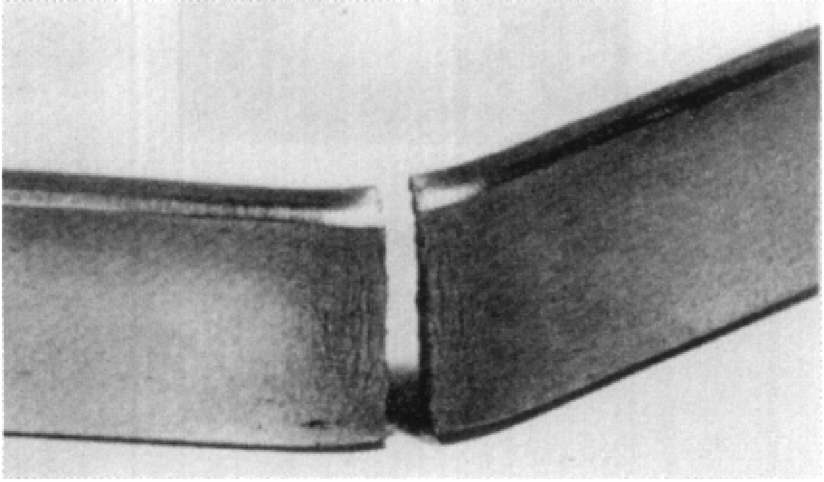

Figure 6: Steel sample after cathodic treatment (× 1). From reference 10.

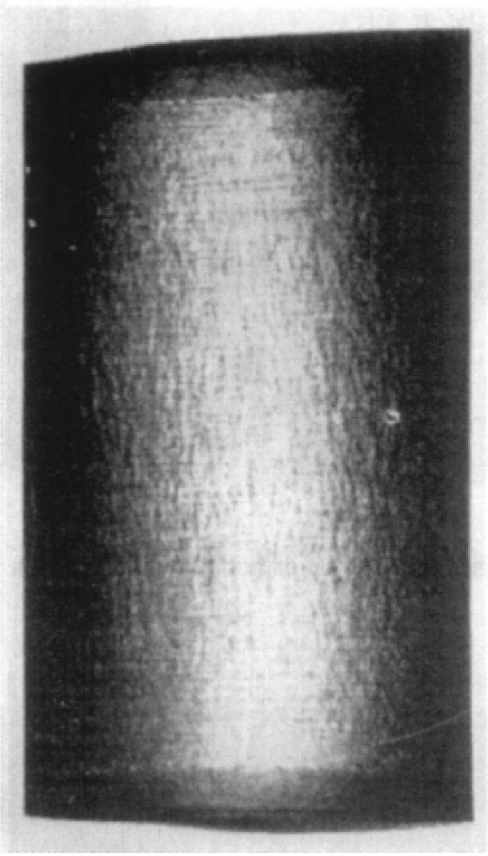

Figure 7: Steel sample with no cathodic treatment (× 3). From reference 10.

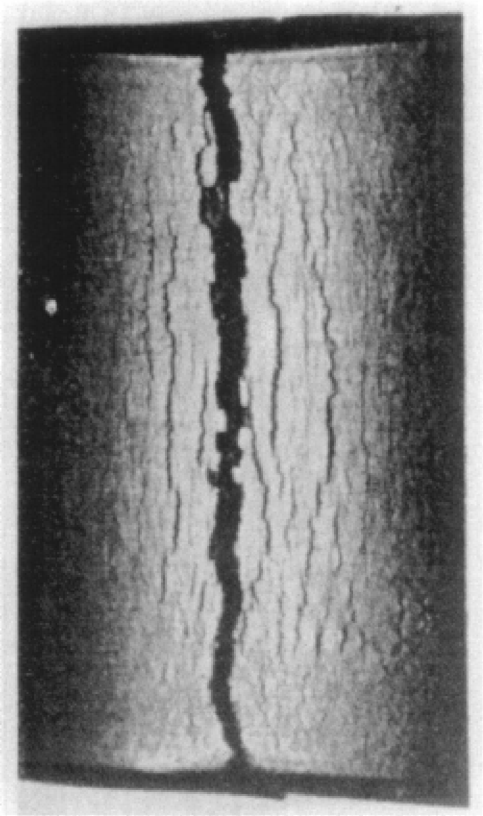

Figure 8: Steel sample after cathodic treatment (× 3). From reference 10.

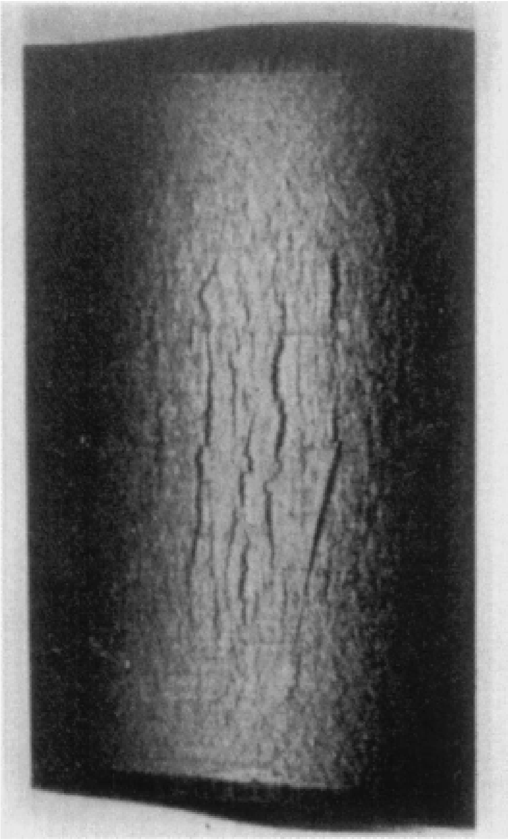

Figure 9: Steel sample after cathodic treatment than heating at 200°C for five minutes (× 3). From reference 10.

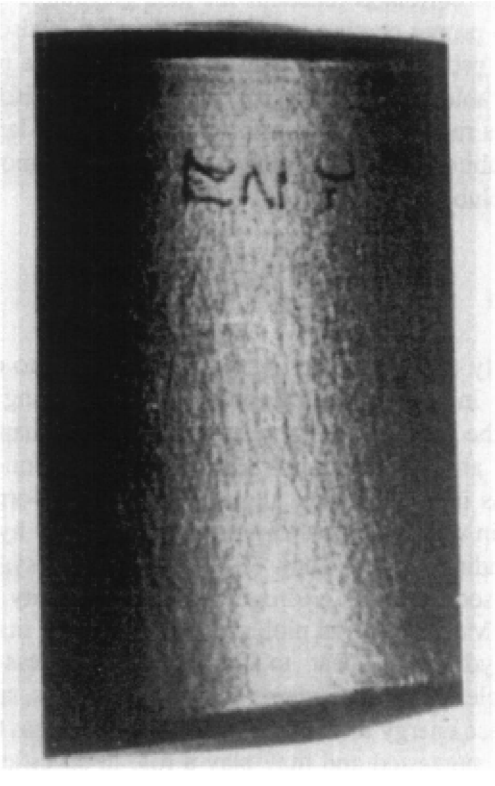

Figure 10: Steel sample after cathodic treatment then heating at 200°C for one hour (× 3). From reference 10.

Platers must be especially aware of hydrogen embrittlement effects since many preplating and plating operations can be potent sources of absorbable hydrogen. Table 1, which lists sources of hydrogen, clearly shows that cathodic cleaning, pickling and electroplating are all culprits. This table also shows why anodic cleaning, which generates no hydrogen, is preferable to cathodic cleaning which generates copious amounts of hydrogen. Since corrosion reactions are also generators of hydrogen, care in choosing the proper coating to prevent corrosion is also quite important. In general, any process producing atomic hydrogen at a metal surface will induce considerable hydrogen absorption in that metal. However, not all the hydrogen atoms released at the surface enter metals; a large fraction combines or recombines to form bubbles of gaseous or molecular hydrogen which is not soluble in metals (9).

MECHANISM

A variety of mechanisms have been proposed to explain hydrogen embrittlement. In fact within a given system, depending on the source of hydrogen and the nature of the applied stress, the mechanism may change. The following are suggested by Birnbaum (1): "Non-hydride forming systems such as iron and nickel alloys which do not form hydrides under the conditions in which they are embrittled fail because hydrogen decreases the atomic bonding (decohesion). In many of these systems the fracture seems to be associated with hydrogen-induced plasticity in the vicinity of the crack tip. Metals such as niobium, zirconium, or titanium, which can form stable hydrides, appear to fracture by a stress-induced hydride formation and cleavage mechanism. Other mechanisms, such as adsorption-decreased surface energy and high-pressure hydrogen gas bubble formation, have also been suggested and may play a role in specific systems" (1).

STEELS

Hydrogen embrittlement effects are most pronounced in steels. These effects can take the form of reduced ductility, ease of crack initiation and/or propagation, the development of hydrogen-induced damage, such as surface blisters and cracks or internal voids, and in certain cases changes in the yield behavior (11). With steels, the problem occurs because of one or more of four primary factors: temperature, microstructure, tensile stresses, and hydrogen content (12). First, room temperature is just about right. An important consequence of the ease of interstitial diffusion (which is the way hydrogen moves about lattices) is the fact that considerable diffusion can

Table 1: Sources of Hydrogen

- ACID TYPE CORROSION

  $Fe + 2HCl \rightarrow FeCl_2 + H_2$

- ELECTROCHEMICAL CLEANING

  ANODE REACTION

  $4\,(OH)^- - 4e \rightarrow 2H_2O + O_2$

  CATHODE REACTION

  $4H^+ + 4e \rightarrow 2H_2$

- PICKLING

  $ACID + METAL \rightarrow SALT + H_2$

- ELECTROPLATING

  CATHODE REACTIONS

  $Ni^{+2} + 2e^- \rightarrow Ni$ METAL

  $2H^+ + 2e^- \rightarrow H_2$

- CONTAINMENT VESSELS FOR H_2
- DAMPNESS IN MOLDS DURING CASTING
- HUMIDITY IN FURNACES DURING HEAT TREATING
- REMNANTS OF DRAWING LUBRICANTS

occur rather quickly even at low temperatures, in fact, even at room temperature. This is one of the circumstances which can lead to hydrogen pickup by metals during aqueous metal finishing operations at the comparatively low temperatures which comprise the range in which water is a liquid (13). Secondly, the microstructure of the plated part must be susceptible to the cracking mechanism and the martensite, bainite, and fine pearlite of quenched and tempered and cold drawn steels can allow the cracking mechanisms to operate at hardnesses down to Rockwell C 24 and lower. Third, tensile stresses are required and even if the part is loaded in compression, tensile stresses can develop and cracks will grow perpendicular to these local tensile stresses. Fourth, a certain amount of hydrogen is required (12).

PREVENTION OF HYDROGEN EMBRITTLEMENT

The prevention of hydrogen embrittlement failure requires a multi-pronged approach:

1. Prevention of hydrogen absorption wherever possible.
2. Elimination of the residual stress in the part before processing.
3. Baking after processing to remove absorbed hydrogen before it can damage the part.

Although beyond the control of the plater, hydrogen absorption can occur because of dampness in molds during casting or from humidity in furnaces during manufacture of the alloy. Baking parts before plating can help minimize stresses and remove absorbed hydrogen. Table 2, a recommendation under development by ASTM, suggests times and tempera-

Table 2: Stress Relief Requirements for High Strength Steels (a)

Tensile Strength MPa	psi	Temp. °C	Time Hours
1000-1400	145,000-203,000	200-230	Minimum 3
1401-1800	203,000-261,000	200-230	Minimum 18
Over 1800	Over 267,000	200-230	Minimum 24

a. From reference 14.

tures (14). Electropolishing before plating could also help; hydrogen entry into sensitive steels may be less than when the surface is stressed (15). Shot peening before plating has also been shown to reduce or even prevent the absorption of hydrogen (7). Other practical steps to minimize hydrogen embrittlement include (16)(17):

- Avoidance of cathodic cleaning, pickling or activation treatments whenever possible, by use of alkaline soak cleaning and anodic cleaning.

- Use of vapor degreasing or solvent cleaning to remove the bulk of grease, oil, or other contaminants before cleaning in aqueous solutions.

- Use of mechanical means (such as tumbling, sand , or grit blasting, vapor blasting, etc.) for oxide and scale removal, rather than pickling.

- Use of inhibited acid pickling solutions. The inhibitors either cut down on the amount of metal dissolved and thereby reduce the amount of hydrogen generated or they can change conditions at the surface so that less of the generated hydrogen enters the metal.

- Use of low embrittling electroplating processes such as special solution compositions and operating conditions which result in either a lower pickup of hydrogen or in a deposit that allows easier removal of the absorbed hydrogen during the baking treatment. Examples include 1) use of fluoborate or Cd-Ti instead of cyanide cadmium, 2) if using cyanide cadmium, plating to a thickness of 5 μm, baking for 3 hours at 190°C to remove hydrogen, and then continuing plating to the required thickness, or 3) use of a more permeable metal such as nickel where possible since hydrogen escapes through nickel far more easily than through zinc or cadmium.

- Use of coating techniques that avoid or minimize hydrogen embrittlement; e.g., vacuum deposited coatings, mechanical plating, and organic coatings.

- Baking after coating to provide hydrogen embrittlement relief. This is a standard practice for removing hydrogen from plated parts and verified in Figure 11 which shows the effect of baking at 149°C on the time-to-failure of notched specimens of 4340 steel heat treated to a strength level of 1590 MPa (230,000 psi). Table 3 lists baking recommendations suggested by ASTM (14).

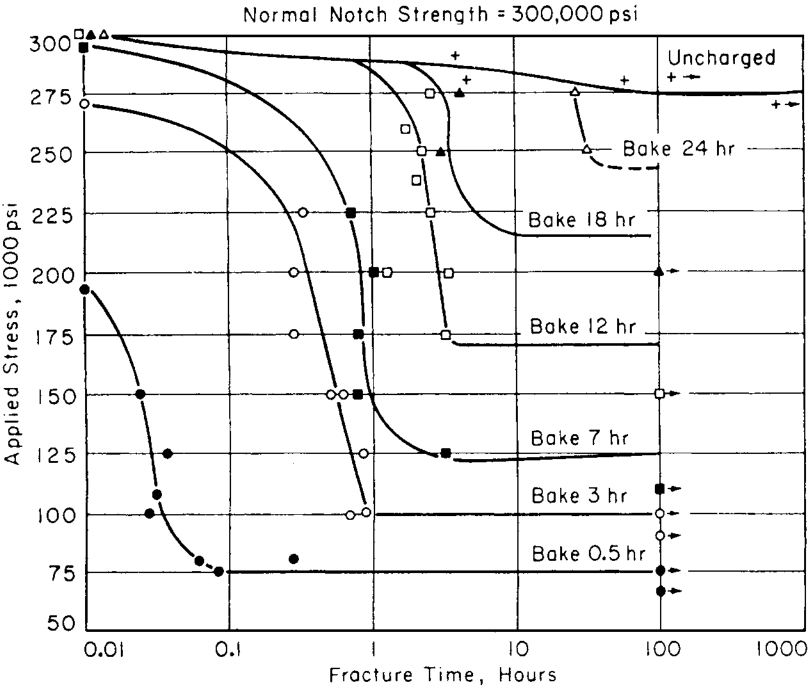

Figure 11: The effect of baking at 149°C on the time-to-failure at a given level of applied stress and stress ratio of notched specimens of 4340 steel heat treated to a strength level of 1586 MPa (230,000 psi). From reference 18. Reprinted with permission of ASM

Table 3: Baking After Plating Recommendations of ASTM (a)

Tensile Strength MPa	psi	Temp. °C	Time Hours
1000-1100	145,000-160,000	190-220	Minimum 8
1101-1200	160,000-174,000	190-220	Minimum 10
1201-1300	174,000-189,000	190-220	Minimum 12
1301-1400	189,000-203,000	190-220	Minimum 14
1401-1500	203,000-218,000	190-220	Minimum 16
1501-1600	218,000-232,000	190-220	Minimum 18
1601-1700	232,000-247,000	190-220	Minimum 20
1701-1800	247,000-261,000	190-220	Minimum 22

a. From reference 14.

Statistically designed screening experiments were conducted to determine the significance of various parameters on the hydrogen content of bright and dull cadmium plated 4340 steel after baking (19)(20). Five variables were investigated: two plating batches, a delay between plating and baking, a delay between baking and measuring, the humidity conditions during this latter delay, and the baking time. Table 4 summarizes the data and shows that for bright cadmium, only the baking time was significant whereas with dull cadmium, the batch was also significant. The reason for this is probably that small changes in concentrations of the solution ingredients, especially carbonate, can have a significant effect on the nature of the deposit from a dull cadmium solution. A delay in baking of 24 hours had no effect on the final hydrogen content. Also, the hydrogen concentration was not altered if the specimens were held for a month at relative humidities of up to 50% after baking.

Table 4: Placket-Burman Results on Removal of Hydrogen From Bright and Dull Cadmium Plated 4340 Steel (a)

Column	Variable	Limits Bright −	Limits Bright +	Factor effect	Limits Dull −	Limits Dull +	Factor effect
x_1	Plating batch	2	1	0.087	1	2	$\boxed{0.145}$
x_2	Time between plating and baking (h)	1	24	0.127	1	24	0.038
x_3	Baking time (h)	8	48	$\boxed{0.350}$	8	20	$\boxed{0.172}$
x_4	Time between baking and measuring (h)	2	690	0.040	2	690	0.065
x_5	Relative humidity (%)**	0	35	0.077	0	50	0.005
	Minimum significant factor effect (90% confidence level)			0.230			0.093

**0% = desiccator; 35% = ambient; 50% = over saturated $Na_2Cr_2O_7$.

a. From reference 19.

Since many practitioners believe that a delay between plating and baking could be important, another experiment was run with just two variables, baking time and delay before baking. Bright cadmium plated specimens were baked for 3 and 72 hours, with delays before baking of 1/4 and 24 hours (20). Data in Table 5 show diffusable hydrogen concentration as a function of baking time and delay before baking. Results clearly reveal that there was no effect on the hydrogen concentration whether or not the baking was done as soon as possible after plating. In spite of these results it is possible that elapsed time between plating and baking can be sufficiently long enough that the migrating hydrogen reaches the critical concentration for crack initiation. No amount of baking will ever repair these cracks; the substrate will have a permanent reduction in yield strength (21).

Table 5: Two Variable, Two-Level Experimental Design and Results for Bright Cadmium Plated 4340 Steel (a)

Trial	Baking Time, h	Time, h	Hydrogen Concentration μA/cm²	Avg.
1	3	1/4	0.88 1.26	1.07
2	3	24	1.08 1.02	1.05
3	72	1/4	0.26 0.31	0.28
4	72	24	0.28 0.31	0.30

a. From reference 20. Background level was 0.22 μA/cm²

Cd-Ti Plating

Cd-Ti plating, an approach to inhibit hydrogen embrittlement, was introduced in the 1960's (22). This technique utilizes a standard cadmium cyanide solution with a sparsely soluble titanium compound plus hydrogen peroxide. When properly operated the deposit contains from 0.1 to 0.5% Ti. This process has been used for coating high strength landing gear actuation cylinders, linkage shafts and threaded rods subjected to high stress (23). A noncyanide electrolyte prepared by adding a predissolved Ti compound to a neutral ammoniacal cadmium solution is also available (24). With this electrolyte, fine-grained Cd-Ti deposits containing 0.1 to 0.7% Ti have been obtained. It is reported that with respect to throwing power, corrosion protection and hydrogen embrittlement, the noncyanide solution is better than the cyanide solution. The Ti compound is stable in the noncyanide solution, so the continuous filtration and frequent analysis required with the Cd-Ti cyanide process are avoided. The process has been used since 1975 for applying protective coatings on high strength structural steel, spring wire and high quality instrument steel (24). Figure 12, which shows hydrogen permeation data for a noncyanide Cd-Ti solution, clearly reveals the influence of Ti in inhibiting hydrogen absorption.

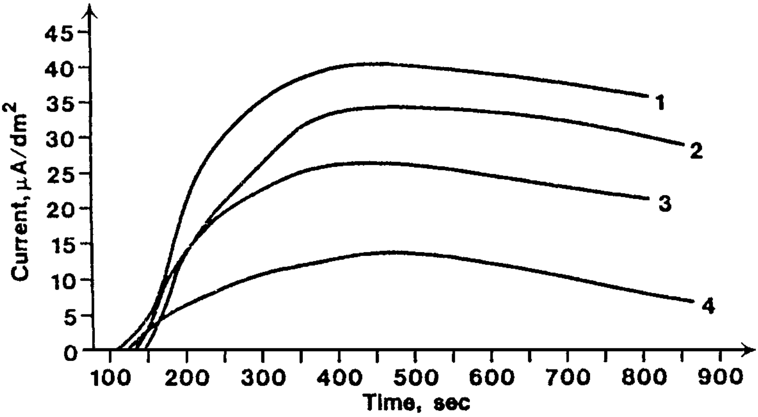

Figure 12: Hydrogen penetration current vs. time in Cd plating solution with (1) no Ti, (2) 0.067 g/l Ti, (3) 2.2 g/l Ti, and (4) 3.1 g/l Ti. From reference 24. Adapted from reference 24.

Mechanical Plating

Mechanical plating is one of the coating techniques available for minimizing hydrogen embrittlement. Also known as peen plating, mechanical plating is an impact process used to apply deposits of zinc, cadmium or tin. It has been a viable alternative to electroplating for the application of sacrificial metal coatings on small parts such as nails, screws, bolts, nuts, washers and stampings for over 30 years (25). Table 6 includes static test data for 1075 steel heat treated to Rc 52-55 before being electroplated with 12.5 μm (0.5 mil) cadmium by normal procedures or by mechanical plating. Parts coated by mechanical plating exhibited no hydrogen embrittlement, whereas, those coated by normal plating exhibited

Table 6: Stress-Endurance Static Tests for Cadmium Plated 1075 Steel (Rc 52-55) Parts (a)

Type of Plating	Group	Less Than 5 Min.	Between 5 min. & 1 hr.	Over one to 240 hrs.	Total No. of Pieces Failed
Electro-plated	Small rings austempered	9	12	One (between 1 & 2 hrs.)	
	Quench and Tempered	30	--	--	30
	Large rings austempered	0	0	0	0
	Quench and tempered	4	23	One(Between 24 & 120 hrs.)	28
Mechanically plated	All groups	0	0	0	0

a. Thirty parts were tested for each condition. For all tests, plating thickness was 12.5 μm (0.5 mil). These data are from reference 26.

various degrees of failure, ranging from 100% failure for small rings which had been quenched and tempered to no failure for large rings which had been austempered. Dynamic testing did reveal that some embrittlement occurred as a result of the mechanical plating process although not as extensive as that obtained with normal plating (26).

Physical Vapor Deposition

One coating technique that eliminates the potential of hydrogen embrittlement is that of physical vapor deposition (PVD), particularly ion plating. PVD processes such as evaporation, sputtering and ion plating are discussed in some detail in the chapter on Adhesion. Since these processes are done in vacuum, the chance of embrittlement by hydrogen is precluded. For production parts, precleaning consists of solvent cleaning followed by mechanical cleaning with dry aluminum oxide grit (27). Therefore, there is no need for costly embrittlement relief procedures nor is there the risk of catastrophic failure due to processing. Ion plated aluminum coatings have been used for over 20 years particularly for aircraft industry applications (28). This aluminum deposit protects better than either electroplated or vacuum deposited cadmium in acetic salt fog and most outdoor environments. Class I coatings, 25 µm (0.001 inch minimum) of ion vapor deposited aluminum have averaged 7500 hours before the formation of red rust in 5 percent neutral salt fog when tested under ASTM-E-117 (29).

Permeation

Since one of the key methods for minimizing hydrogen embrittlement is the use of a barrier coating, the influence of various coatings on the permeability of hydrogen is of importance. Thin layers of either Pt, Cu, or electroless nickel decrease permeability of hydrogen through iron (30). The coatings do not have to be thick or even continuous to be effective suggesting that a catalytic mechanism is responsible for the marked reduction in hydrogen permeation through the iron. Au (31)(32), Sn and Sn-Pb alloy coatings are also very effective permeation barriers (33)-(35). Lead coatings are effective in preventing hydrogen cracking on a variety of steels in many different environments (36)-(38). Permeation data presented in Figures 13 through 15 show that:

- A Pt coating of only 0.015 µm was very effective in reducing hydrogen permeation through iron (Figure 13).

- Cu was noticeably more effective than Ni in reducing the rate of hydrogen uptake by iron (Figure 14).

- With 1017 steel, brush plating with 70Pb-30Sn noticeably reduced the permeability (Figure 15). An imperfect brush plated zinc coating was also quite effective in reducing permeability.

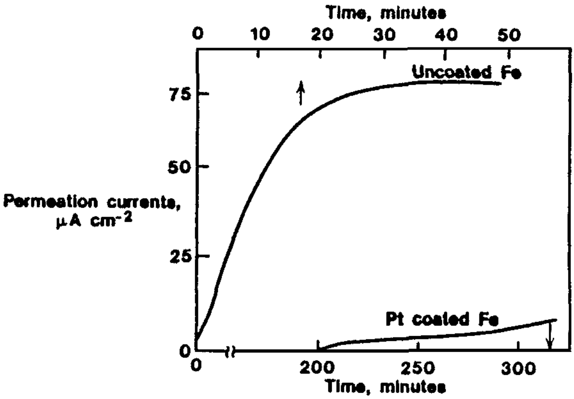

Figure 13: Effect of a platinum coating (0.015 µm thick) on the permeation of hydrogen through Ferrovac E iron membranes. Charging current density was 2 mA/cm². Charging solution was 0.1 N NaOH plus 20 ppm As^{3+}. Adapted from reference 30.

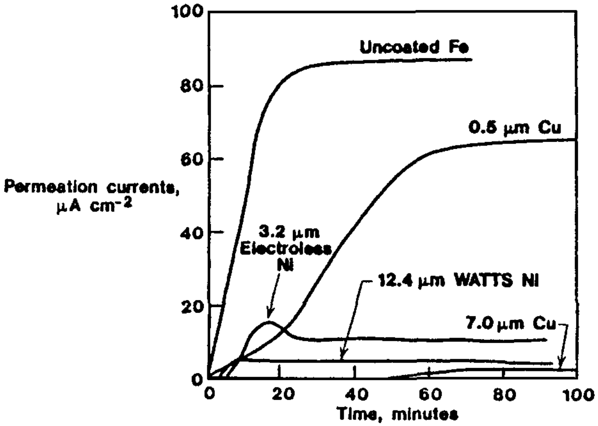

Figure 14: Effect of copper, nickel and electroless nickel coatings on the permeation of hydrogen through Ferrovac E iron membranes. Charging current density was 2 mA/cm². Charging solution was 0.1 N NaOH plus 20 ppm As^{3+}. Adapted from reference 30.

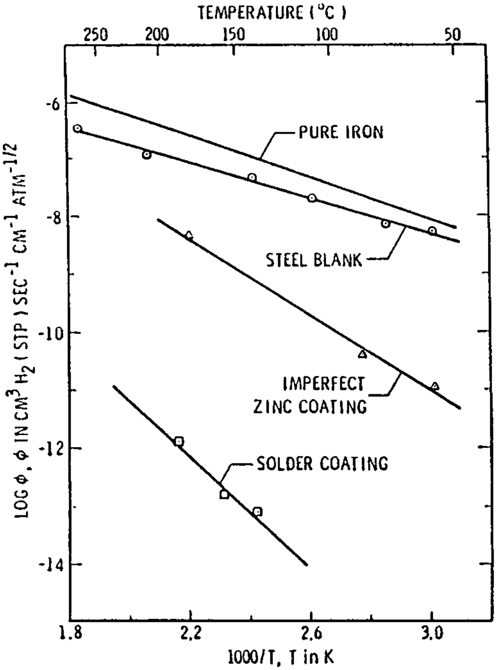

Figure 15: Brush plating as a means of reducing hdyrogen uptake and permeation in 1017 steel. Adapted from reference 33.

Extensive work for NASA has shown the effectiveness of Cu and Au in reducing the permeability of hydrogen. For example, electrodeposited nickel is highly susceptible to hydrogen environment embrittlement (HEE) (32)(39)(40). Both ductility and tensile strength of notched specimens show reductions up to 70 percent in 48.3 Mpa (7000 psi) hydrogen when compared with an inert environment at room temperature. Annealing at 343°C minimizes the HEE of electrodeposited nickel regardless of the current density used to deposit the nickel. Another approach to prevent HEE of electrodeposited nickel is to coat the nickel with copper or gold. Tensile tests conducted to determine the effectiveness of 80 μm thick copper and 25 μm thick gold are summarized in Table 7. Both coatings allowed the electrodeposited nickel to retain its ductility in high pressure hydrogen (32).

Since metallurgically prepared nickel alloys are also notoriously susceptible to hydrogen embrittlement, NASA utilizes an electrodeposited copper layer (150 um) to protect the inner surface of a four ply nickel alloy bellows from contacting a hydrogen atmosphere. This bellows is used in the Space Shuttle engine turbine drive and discharger ducts prior to forming (41).

Table 7: Effect of Copper and Gold Coatings on the Tensile Properties of Unnotched Electrodeposited Nickel Specimens in High-Pressure Hydrogen At Room Temperature (a)

Coating	Test Environ.	Test Pressure		Ultimate Tensile Strength		Elongation (%)	Reduction Area (%)
		MPa	psi	MPa	psi		
Uncoated	He	8.3	1,200	538	78,000	23	90
Uncoated	H_2	8.3	1,200	503	73,000	5	30
Copper(b)	H_2	48.3	7,000	572	83,000	25	91
Gold (c)	H_2	8.3	1,200	531	77,000	25	89

a. These data are from reference 32.
b. Copper was 75 µm (3 mil) thick.
c. Gold was 25 µm (1 mil) thick.

Electroless Copper

An excellent application of materials science principles is the work by researchers at AT & T Bell Laboratories on electroless copper. By utilizing a variety of sophisticated analytical techniques including inert gas fusion analysis, ion microprobe analysis, thin film ductility measurements, and scanning and transmission electron microscopy they showed that hydrogen is responsible for the lower ductility noted in electroless copper deposits when compared with electrodeposited copper films (6)(42)-(49). They attributed this ductility loss to hydrogen embrittlement contrary to the common notion that physical properties of Group IB metals (copper, silver, and gold) are insensitive to hydrogen (44). This work should be generally applicable to other electrodeposited and electroless films in which the deposition process involves a simultaneous discharge of both metal and hydrogen ions (6).

Electroless copper deposition is used extensively in the fabrication of printed wiring boards. Since these deposits are often subjected to a hot solder bath during the printed wiring board manufacturing process, good ductility is required to withstand thermal shock. An item of concern with electroless copper deposits is their ductility which is generally much poorer (~ 3.5%) than that of electrolytic copper (12.6 to 16.5%) (6). This loss in film ductility for electroless copper deposits has been attributed to a high (10^4 atm.) pressure developed because of hydrogen gas bubbles in analogy to the pressure effect in classical hydrogen embrittlement (6). In the electroless copper deposition process, the formation of hydrogen gas is an integral part of the overall deposition reaction:

$$Cu(II) + 2HCHO + 40H \rightarrow Cu + 2HCOO + 2H_{2}0 + H_2$$

Some of the hydrogen atoms and/or molecules can be entrapped in the deposit in the form of interstitial atoms or gas bubbles (48). By contrast, in the case of electrolytic copper deposition, hydrogen evolution can be avoided by choosing the deposition potential below the hydrogen overpotential to prevent hydrogen reduction. This cannot be done with electroless copper deposition since hydrogen reduction is an integral part of the deposition reaction.

Table 8, which lists the concentration ranges of impurity elements found in an electroless copper deposit, shows that hydrogen content is disproportionately high compared to the other elements (46). Some of this hydrogen can be removed by annealing at relatively low temperatures and this results in an improvement in ductility. Figure 16 shows the variation of ductility and hydrogen content with annealing time at 150°C in nitrogen. The ductility improves with annealing time and reaches a nearly constant

Table 8: Inclusions in Electroless Copper Deposits (a)

Element	ppm, Weight	ppm, Atomic
H	30-200	1900-12700
C	90-800	480-4230
O	70-250	280-990
N	20-110	90-500
Na	20-70	55-190

a. These data are from reference 46.

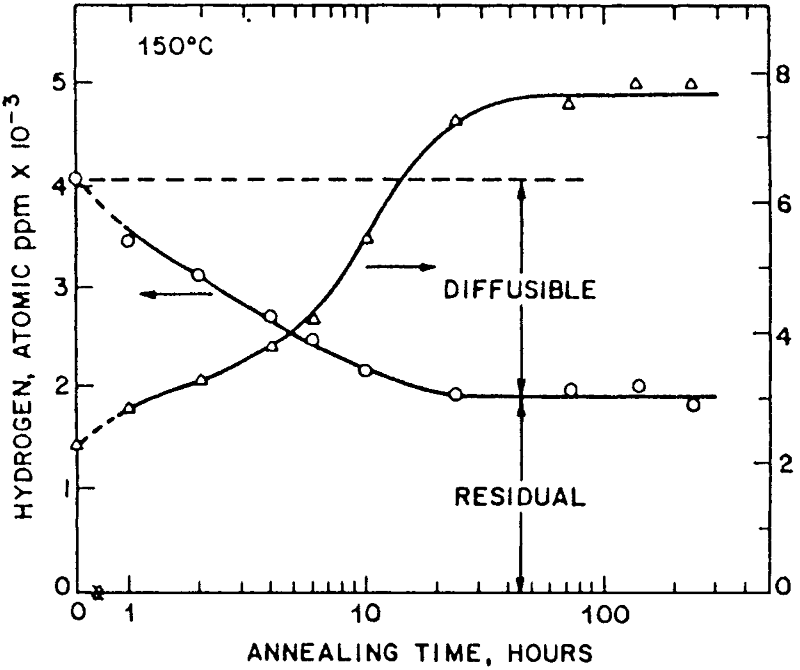

Figure 16: Variation of hydrogen content and ductility with annealing time at 150°C for an electroless copper deposit. From reference 46. Reprinted with permission of The Electrochemical Soc.

level after 24 hours. In somewhat similar fashion, the hydrogen content decreases initially and becomes constant after the same length of time. Inspection of the hydrogen curve reveals that two kinds of hydrogen are present in the deposit, "diffusable hydrogen" which escapes on annealing, and "residual hydrogen" which is not removed by annealing (46). The close correlation between the loss of hydrogen and improvement in ductility shown in Figure 16 is further demonstrated by a cathodic charging experiment in which an annealed deposit containing no diffusable hydrogen was made a cathode in an acidic solution to evolve hydrogen for an extended period of time, and the diffusable hydrogen and ductility remeasured (46). The results are presented in Table 9.

This extensive work by researchers at AT & T Bell Laboratories has led them to conclude that hydrogen inclusion introduces two sources of embrittlement into electroless copper. The first one is the classical hydrogen embrittlement by the pressure effect and the second is the introduction of void regions, which promote the ductile fracture by the void coalescence mechanism. The former embrittlement can be removed by annealing at 150°C but the latter remains constant (47).

Table 9: Cathodic Charging Experiment With Electroless Copper Deposits (a)

Condition	Ductility %	Diffusable Hydrogen ppm, Atomic
As deposited	2.1	2780
After annealing (b)	6.5	0
After charging	3.8	2360
After reannealing (b)	6.4	0

a. These data are from reference 46. Cathodic charging conditions: 0.05M H_2SO_4, 0.001M As_2O_3, (10mA/cm^2, 15 hours)

b. Annealing was done at 150°C for 24 hours.

Chemical Milling

Chemical milling has evolved as a valuable complement to conventional methods of metal removal. Any metal that can be dissolved chemically in solution can be chemically milled. Aluminum, beryllium, magnesium, titanium, and various steel and stainless steel alloys are among those most commonly milled although refractory metals such as molybdenum, tungsten, columbium, and zirconium, can also be handled. Parts can be flat, preformed, or irregular, and metal can be removed from selected areas or the entire surface (50).

Chemical milling of steels, stainlesses and high-temperature alloys typically requires extremely corrosive raw-acid mixtures. In spite of the fact that much hydrogen is generated during the process, milled parts suffer little or no degradation. Data in Table 10 summarize the influence of chemical milling on the tensile properties of various alloys. In most cases, no degradation was noted. With 4340, some embrittlement was obtained with chemically milled specimens, but properties were restored by aging at room temperature.

Titanium alloys are chemically milled primarily to provide a maximum strength-to-weight ratio. As with steels, various acids are used for milling,therefore, hydrogen is generated (50)(59)-(61). Since titanium and its alloys are susceptible to hydrogen embrittlement (Figure 17) the amount of hydrogen picked up when these materials are chemically milled is of major concern (2). In titanium structures, hydrogen can concentrate at the surface causing a reduction in surface sensitive properties. The most important factors governing the amount of hydrogen absorbed are the composition and metallurgical structure of the alloy, the composition and temperature of the etching solution, the etching time, the sequence in which the parts fit into the milling cycle, whether the parts are etched on one or both sides, and the mass of material remaining after etching. For example, hydrogen pickup is much greater when specimens are milled from two sides rather than just one. Figure 18 contains data for Ti-6Al-6V-2Sn, showing that absorption is a function of the ratio of chemically milled surface to final volume and not of the amount of metal removed by milling (59). Table 11 summarizes data on hydrogen absorption for various titanium alloys.

TESTS FOR HYDROGEN EMBRITTLEMENT

A variety of tests are available for assessing hydrogen embrittlement but these will not be covered here. For those interested in these tests, references 63 and 64 provide a good starting point.

Table 10: Influence of Chemical Milling on the Tensile Properties of Some Alloy Steels

Alloy	Tests	Results	Ref.
4340, D6ac	Sustained Load (1800 MN/m^2)	No Hydrogen embrittlement.	51
4349, H-11, 17-7 PH	Sustained Load	Embrittled, but recovery occurred with 1 week after storage at room temperature or after 49 hours at room temperature followed by a 4 hour bake at 190°C.	
4340	Bend	Removal of 250 or 500 µm by chemical milling resulted in hydrogen embrittlement. Ductility was restored by aging at room temperature for 8 to 33 hours.	52
1Cr-Mo Steel 3CR-Mo-V Steel 5CR-Mo-V Steel	Sustained Load	No adverse effects.	53
18% Ni Maraging Steel	Sustained Load (2000 MN/m^2)	No adverse effects.	54
301 Stainless	Tensile	No adverse effects.	55
Rene 41	Tensile	Higher strengths than for base-metal controls.	51
Rene 41	Tensile	Slight reduction in tensile strength at 760°C, no adverse effects between 760°C and 980°C. Some reduction in elongtion: 15% at 27°C, 40% at 760°C and 20% at 980°C.	56
Inconel X	Tensile and Stress—Rupture	No adverse effects.	57
PH 14-8	Tensile	Some reduction in properties, but this was attributed to differences in specimen thickness.	58

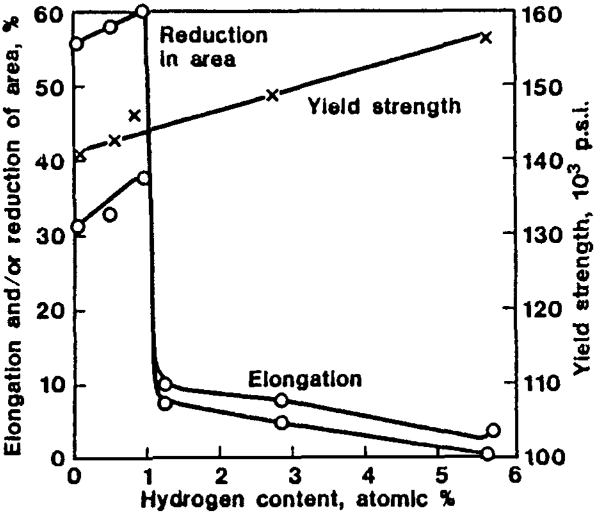

Figure 17: Tensile properties of Ti-8Mn as a function of hydrogen content. Adapted from reference 4.

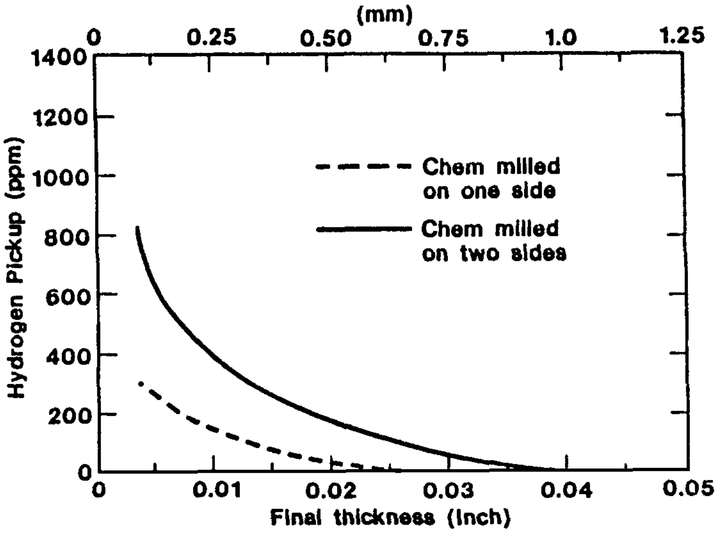

Figure 18: Hydrogen absorption vs. depth of cut for chemically milled Ti-6Al-6V-2Sn. Adapted from reference 59.

Table 11: Influence of Chemcial Milling on the Hydrogen Content of Various Titanium Alloys

	Metal Removed		Hydrogen, ppm			
Alloy	µm	inch	Before	After	Change	Ref.
Ti-6Al-4V	125	.005	50	46	-4	59
	250	.010	29	39	10	
	500	.020	29	48	19	
	750	.030	29	68	29	
	750	.030	78	36	-42	
Ti-5Al-2.5Sn	250	.010	34	37	3	59
	500	.020	34	35	1	
	750	.030	34	36	2	
Ti-8Al-1Mo-1V	250	.010	46	39	-7	59
	500	.020	46	45	-1	
	750	.030	46	42	-4	
Ti-15V-3Cr-3Al-2Sn	5	.0002	-	-	0	62
	35	.0014	-	-	11	
	75	.0030	-	-	50	

REFERENCES

1. H.K. Birnbaum, "Hydrogen Embrittlement", *Encyclopedia of Materials Science and Engineering*, M.B. Bever, Editor, Pergamon Press, 2240 (1986)

2. M.R. Louthan, Jr., "The Effect of Hydrogen on Metals", *Corrosion Mechanisms*, F. Mansfeld, Editor, Marcel Dekker Inc., NY (1987)

3. E.A. Groshart, "Design and Finish Requirements of High Strength Steels", *Metal Finishing* 82, 49 (March 1984)

4. P. Bastien and P. Azou, "Effect of Hydrogen on the Deformation and Fracture of Iron and Steel in Simple Tension", *Proceedings of the First World Metallurgical Congress*, ASM (1951)

5. D. Nguyen, A.W. Thompson and I.M. Bernstein, "Microstructural Effects on Hydrogen Embrittlement in a High Purity 7075 Aluminum Alloy", *Acta. Metall.*, 35, 2417 (1987)

6. S. Nakahara and Y. Okinaka, "Microstructure and Ductility of Electroless Copper Deposits", *Acta Metall.*, 31, 713 (1983)

7. L.J. Durney, "Hydrogen Embrittlement: Baking Prevents Breaking", *Products Finishing*, 49, 90 (Sept 1985)

8. H. Geduld, *Zinc Plating*, ASM International, 203 (1988)

9. H.C. Rogers, "Hydrogen Embrittlement", *Science*, 159, 1057 (1968)

10. L.E. Probert and J.J. Rollinson, "Hydrogen Embrittlement of High Tensile Steels During Chemical and Electrochemical Processing", *Electroplating and Metal Finishing*, 14, 396 (Nov 1961)

11. I.M. Bernstein and A.W. Thompson, "Hydrogen Embrittlement of Steels", *Encyclopedia of Materials Science and Engineering*, M.B. Bever, Editor, Pergamon Press, 2241 (1988)

12. C.D. Beachem, "Mechanisms of Cracking of Hydrogen-Charged (Hydrogen-Embrittled) Aerospace Materials", *Proceedings AESF Aerospace Symposium* (Jan 1989)

13. H.J. Read, "The Metallurgical Aspects of Hydrogen Embrittlement in Metal Finishing", *47th Annual Technical Proceedings*, AES, 110 (1960)

14. A.W. Grobin, "Other ASTM Committees and ISO Committees Involved in Hydrogen Embrittlement Test Methods", *Hydrogen Embrittlement: Prevention and Control,* ASTM STP 962, L. Raymond, Editor, ASTM, Philadelphia, PA, 46 (1988)

15. C.L. Faust, "Electropolishing Carbon and Low Alloy Steels-Part 1", *Metal Finishing*, 81, 47 (May 1983)

16. E.T. Clegg, "Hydrogen Embrittlement Coverage by U. S. Government Standardization Documents", *Hydrogen Embrittlement: Prevention and Control*, ASTM STP 962, L. Raymond, Editor, ASTM, Philadelphia, PA, 37 (1988)

17. A.W. Thompson, "Metallurgical Characteristics of Hydrogen Embrittlement", *Plating & Surface Finishing*, 65, 36 (Sept 1978)

18. A.R. Troiano, "The Role of Hydrogen and Other Interstitials on the Mechanical Behavior of Metals", *Trans. American Society for Metals*, 52, 54 (1960)

19. D.A. Berman, "Removal of Hydrogen From Cadmium Plated High Strength Steel by Baking-A Statistically Designed Study", Report No. NADC-82238-60 (Nov 1982), Naval Air Development Center, Warminster, PA

20. D.A. Berman, "The Effect of Baking and Stress on the Hydrogen Content of Cadmium Plated High Strength Steels", AD-A166869 (Dec 1985), Naval Air Development Center, Warminster, PA

21. A.W. Grobin, Jr., "Hydrogen Embrittlement Problems", *ASTM Standardization News*, 18, 30 (March 1990)

22. K. Takata, Japanese patents SHO-35 18260 (1960) and SHO-38 20703 (1963)

23. AMS-2419A, "Cadmium-Titanium Alloy Plating", *Soc. of Automotive Engineers*, Warrendale, PA (1979)

24. W. Sheng-Shui, C. Jing-Kun, S. Yuing-Mo and L. Jin-Kuel, "Cd-Ti Electrodeposits From a Noncyanide Bath", *Plating & Surface Finishing*, 68, 62 (Dec 1981)

25. R.N. Holford, Jr., "Five-Year Outdoor Exposure Corrosion Comparison", *Metal Finishing*, 86, 17 (July 1988)

26. L. Coch, "Plating Fasteners, Avoiding Embrittlement", *Products Finishing*, 51, 56 (May 1987)

27. V.L. Holmes, D.E. Muehlberger and J.J. Reilly, "The Substitution of IVD Aluminum for Cadmium", ESL-TR-88-75, *Engineering & Services Laboratory*, Tyndall Air Force Base, FL (Aug 1989)

28. E.R. Fannin and D.E. Muehlberger, "Ivadizer Applied Aluminum Coating Improves Corrosion Performance of Aircraft", McDonnell Aircraft Company, MCAIR 78-006 (1978)

29. D.E. Muehlberger, "Ion Vapor Deposition of Aluminum-More Than Just a Cadmium Substitute", *Plating & Surface Finishing*, 70, 24 (Nov 1983)

30. S.S. Chatterjee, B.G. Ateya and H.W. Pickering, "Effect of Electrodeposited Metals on the Permeation of Hydrogen Through Iron Membranes", *Metallurgical Transactions A*, 9A, 389 (1978)

31. T-P. Perng, M.J. Johnson and C.L Alstetter, "Hydrogen Permeation Through Coated and Uncoated Waspalloy", *Metallurgical Transactions A*, 19A, 1187 (1988)

32. W.T. Chandler, R.J. Walter, C.E. Moeller and H.W. Carpenter, "Effect of High-Pressure Hydrogen on Electrodeposited Nickel", *Plating & Surface Finishing* 65, 63 (May 1978)

33. S.L. Robinson, W.A. Swansiger and A.D. Andrade, "The Role of Brush Plating in Future Hydrogen Storage and Transmission Systems", *Plating & Surface Finishing* 66, 46 (August 1979)

34. D.R. Begeal, "The Permeation and Diffusion of Hydrogen and Deuterium Through Rodar, Tin-Coated Rodar and Solder-Coated Rodar", *J. Vac. Sci. Technol.*, 12, 405 (Jan/Feb 1975)

35. J. Bowker and G.R. Piercy, "The Effect of a Tin Barrier on the Permeability of Hydrogen Through Mild Steel and Ferritic Stainless Steel", *Metallurgical Transactions A*, 15A, 2093 (1984)

36. L. Freiman and V. Titov, "The Inhibition of Diffusion of Hydrogen Through Iron and Steel by Surface Films of Some Metals", *Zhur. Fiz. Khim.*, 30, 882 (1956)

37. I. Matshushima and H.H. Uhlig, "Protection of Steel From Hydrogen Cracking by Thin Metallic Coatings", *J. Electrochem. Soc.*, 113, 555 (1966)

38. H. Tardif and H. Marquis, "Protection of Steel From Hydrogen by Surface Coatings", *Canadian Metallurgical Quarterly*, 1, 153 (1962)

39. R.P. Jewett, R.J. Walter, W.T. Chandler and R.P. Frohmberg, "Hydrogen Environment Embrittlement of Metals", *NASA CR-2163*, (Mar 1963)

40. W.T. Chandler and R.J. Walter, "Hydrogen Embrittlement", *ASTM STP 543*, American Society for Testing and Materials, Philadelphia, PA, 182 (1974)

41. "Electroplating Offers Embrittlement Protection", *NASA Tech Briefs*, p 140 (Spring 1979)

42. S. Nakahara and Y. Okinaka, "Transmission Electron Microscopic Studies of Impurities and Gas Bubbles Incorporated in Plated Metal Films", *Properties of Electrodeposits: Their Significance and Measurement*, R. Sard, H. Leidheiser, Jr., and F. Ogburn, Editors, The Electrochemical Soc., Pennington, NJ, (1975)

43. Y. Okinaka and S. Nakahara, "Hydrogen Embrittlement of Electroless Copper Deposits", *J. Electrochem. Soc.*, 123, 475 (1976)

44. S. Nakahara and Y. Okinaka, "On the Effect of Hydrogen on Properties of Copper", *Scripta Metall.*, 19, 517 (1985)

45. J.E. Graebner and Y. Okinaka, "Molecular Hydrogen in Electroless Copper Deposits", *J. Appl. Physics*, 60, 36 (July 1986)

46. Y. Okinaka and H.K. Straschil, "The Effect of Inclusions on the Ductility of Electroless Copper Deposits", *J. Electrochem. Soc.*, 133, 2608 (1986)

47. S. Nakahara, "Microscopic Mechanism of the Hydrogen Effect on the Ductility of Electroless Copper", *Acta Metall.*, 36, 1669 (1988)

48. S. Nakahara and Y. Okinaka, "The Hydrogen Effects in Copper", *Materials Science and Engineering*, A, 101, 227 (1988)

49. S. Nakahara., Y. Okinaka, and H.K. Straschil, "The Effect of Grain Size on Ductility and Impurity Content of Electroless Copper Deposits", *J. Electrochem. Soc., 136*, 1120 (1989)

50. J.W. Dini, "Fundamentals of Chemical Milling", *American Machinist*, 128, 113 (July 1984)

51. C. Micillo, "Advanced Chemical Milling Processes", AFML-TR-68-237, or AD 847070 (August 1968)

52. R.L. Jones, "A New Approach to Bend Testing for the Determination of Hydrogen Embrittlement of Sheet Materials", AD 681765 (June 1961)

53. Anon., "The Chemical Contouring of 3% Chromium--Molybdenum-Vanadium and 5% Chromium-Molybdenum-Vanadium High Strength Steel", *Bristol Aerojet England*, BR-ARC-CP-811 (March 1964)

54. E.C. Kedward and P.F. Langstone, "Chemical Contouring of 18 Percent Nickel Maraging Steel", *Sheet Metal Industries*, London, 46, 473 (June 1969)

55. R.L. Jones and P. Bergstedt, "Compilation of Materials Research Data, Fourth Quarterly Progress Report-Phase 1", *General Dynamics*, AD 273065 (Dec 1961-Feb 1962)

56. E. Howells, "Taper Chemical Milling of Rene 41 Tubes", Boeing Co., Seattle, Wash., MDR-2-14969 (March 1962)

57. S.J. Ketcham, "Chemical Milling of Alloy Steels", Naval Air Engineering Center, NAEC-AML-2418 or AD 631952 (March 1966)

58. B. Chapman and J. Derbyshire Jr., "Confirmation of the Close Tolerance Chem-Mill Process to PH 14-8 Mo Steel for the Apollo Heat Shield", North American Aviation, SDL 435 (Nov. 6, 1963)

59. C. Micillo and C.J. Staebler Jr., "Chemical Milling Using Cut Maskant Etching Masks", *Photochemical Etching*, 3, 4 (June 1968)

60. CHEMICAL MILLING, W.T. Harris, Oxford Univ. Press, New York (1976)

61. J.W. Dini, "Chemical Milling", *International Metallurgical Reviews*, 20, 29 (1975)

62. R. Messler Jr. and J. Masek, "Thermal Processing, Cleaning, Descaling and Chemical Milling of Ti-15V-3Cr-3Al-3Sn Titanium Alloy", TMS/AIME Paper F80-15 (1979)

63. L. Raymond, "Evalaution of Hydrogen Embrittlement", *Metals Handbook, Ninth Edition*, Vol 13, Corrosion (1987), American Society for Metals, Metals Park, Ohio

64. *Hydrogen Embrittlement: Prevention and Control*, ASTM STP 962, L. Raymond, Editor, American Society for Testing and Materials, Philadelphia, PA (1988)