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**HYDROGEN-INDUCED, DELAYED, BRITTLE FAILURES
OF HIGH-STRENGTH STEELS**



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INTRODUCTION

DMIC Memorandum No. 180, "The Problem of Hydrogen in Steel", October 1, 1963, was written with the intent of helping the steel user determine if he has a problem of delayed, brittle failure associated with hydrogen in steel, particularly high-strength steel. The effects of hydrogen on the mechanical properties of steel are dealt with, and the general behavior of material susceptible to delayed, brittle failure is described. The most noteworthy characteristic of delayed, brittle failures induced in steel by hydrogen is the loss in ability to support a sustained load. Also, possible sources of hydrogen in steel and the types of tests useful in determining the susceptibility to delayed failure are outlined.

The present report discusses in detail the factors that influence the susceptibility of high-strength steels to this type of failure.

EFFECT OF THE COMPOSITION OF THE MATERIAL

Many types of steel, including types with a wide variety of alloying additions, comprising both substitutional and interstitial elements, have been examined for resistance to hydrogen embrittlement and hydrogen-induced, delayed, brittle failure. No alloying element has been able to eliminate the propensity toward delayed, brittle failure, and none has been truly effective in retarding failures of this type. All ferritic and martensitic steels investigated under test conditions that promote delayed, brittle failure have been susceptible to this type of failure. However, no instances of hydrogen-induced, delayed, brittle failure of an austenitic steel is known to the authors. Even when severe cathodic charging conditions have been used, no delayed failure and relatively little loss in ductility have been encountered with austenitic steels. However, when austenitic steels are processed so that part of the austenite is transformed to the body-centered cubic form (by cold work or by low-temperature treatment) so that they are no longer fully austenitic, they too become susceptible to such failures. Thus, in the same material, a change in structure can alter what is apparently a completely resistant material into one that is readily susceptible, without change in composition. This has been demonstrated in chromium-nickel, straight-nickel, and manganese austenitic steels. It would seem, then, that the resistance of austenitic materials to this phenomenon is the result of the face-centered cubic structure and not differences in composition.

Because many alloy systems had been investigated and hydrogen embrittlement had been found only in body-centered cubic transition metals, a number of investigators inferred that no face-centered cubic metal can be embrittled by hydrogen: for example, see Reference 1*. However, Eisenkolb and Ehrlich⁽²⁾ discovered that nickel could become embrittled by hydrogen, so the rule is not universal. Later, Blanchard and Troiano⁽³⁾ verified the embrittlement of nickel and also found that certain nickel-base, nickel-iron alloys were embrittled by hydrogen when charged for several hours at a high current density.

*References appear at the end of the report.

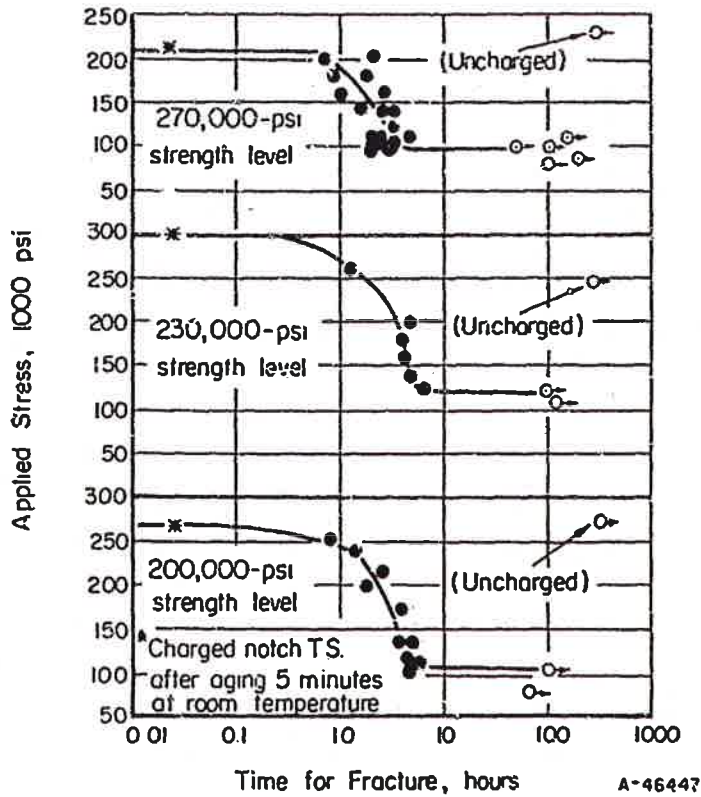


FIGURE 1. DELAYED-FAILURE TESTS ON SAE-AISI 4340 STEEL HEAT TREATED TO SEVERAL STRENGTH LEVELS, SHOWING THE EFFECT OF HYDROGEN⁽⁵⁾

Fixed charging conditions, aged 5 minutes, sharp-notch specimens.

Case Institute of Technology Charging Condition A:

- Electrolyte: 4 per cent H_2SO_4 in water
- Poison: None
- Current density: 20 ma/in.²
- Charging time: 5 minutes
- Aging time: Measured from end of charging to start of test.

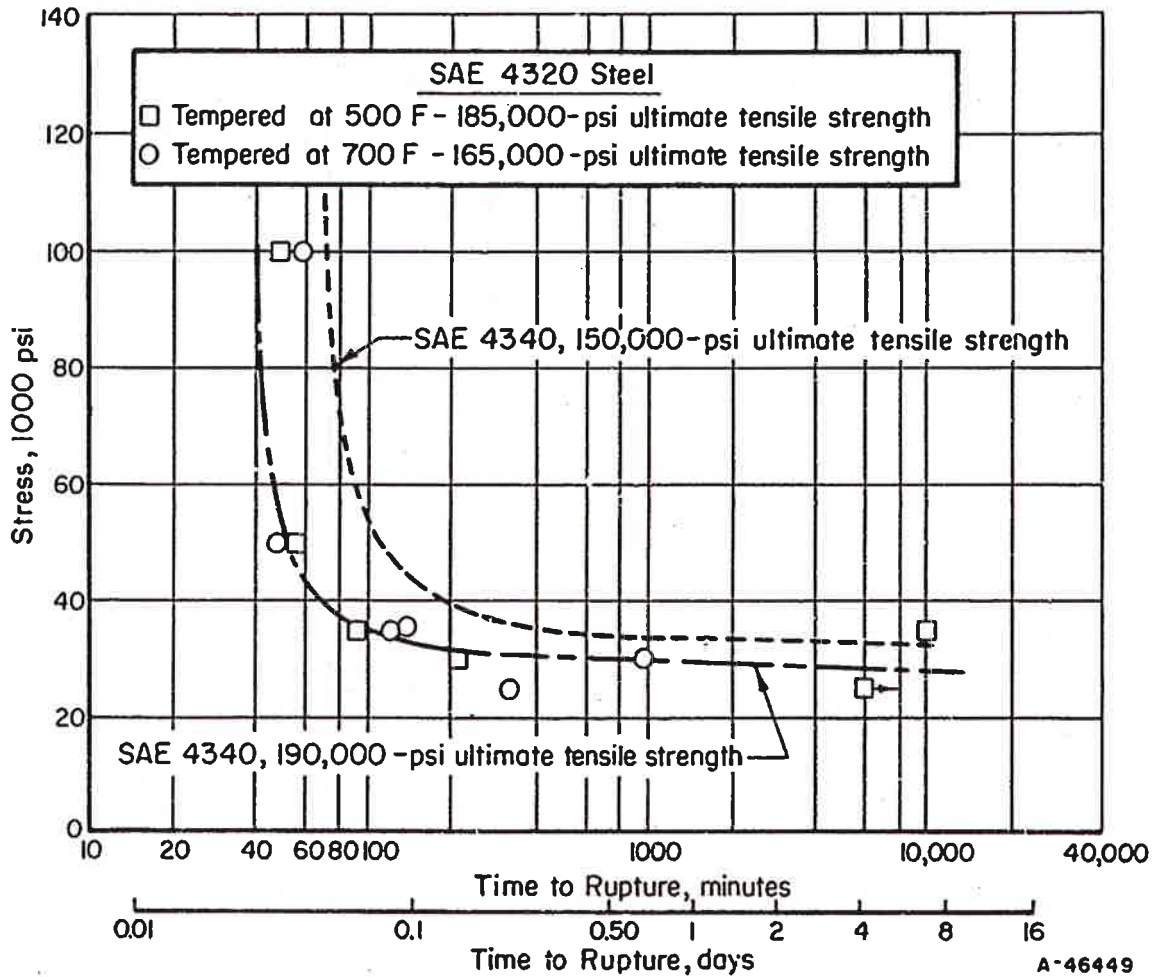


FIGURE 3. DELAYED-FAILURE CHARACTERISTICS OF AN SAE 4320 STEEL DURING CATHODIC CHARGING UNDER STANDARDIZED CONDITIONS⁽⁸⁾

Lines representing characteristics of SAE 4340 steel have been added for comparison. Battelle Charging Condition A, as given in Figure 2.

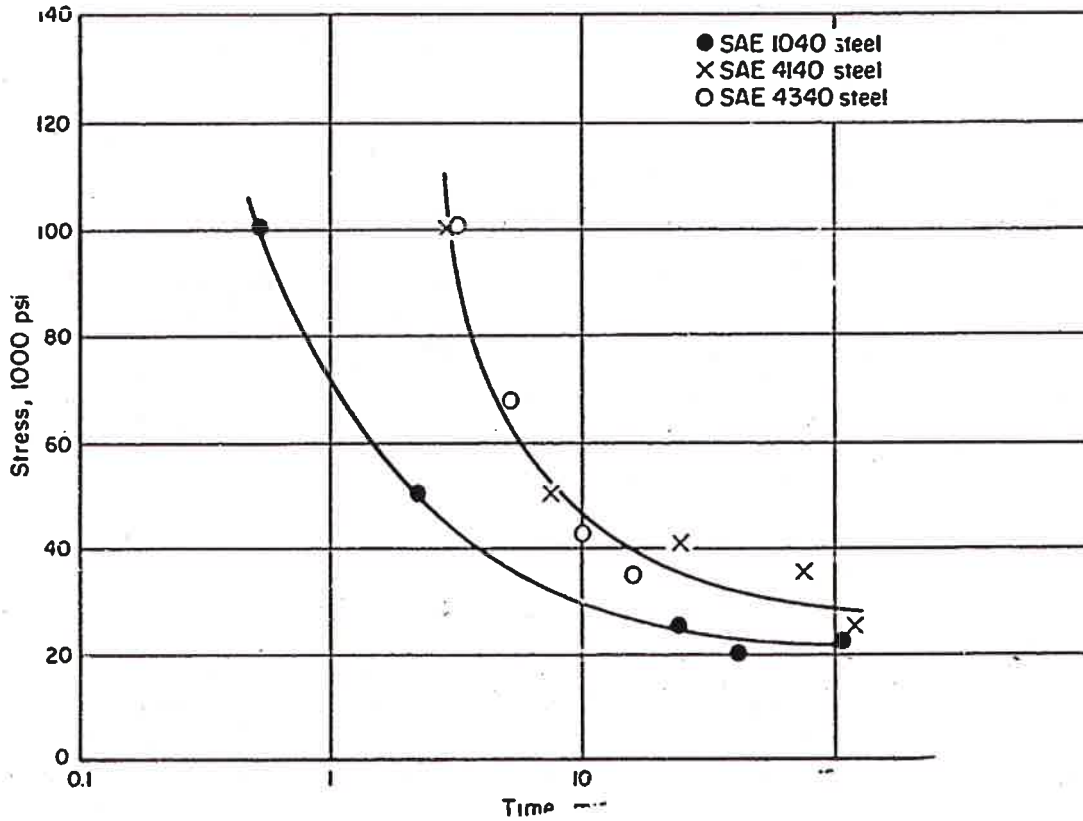


FIGURE 5. FAILURE TIME AS A FUNCTION OF APPLIED STRESS FOR SAE 1040, 4140, AND 4340 STEELS HEAT TREATED TO APPROXIMATELY 270,000-PSI ULTIMATE TENSILE STRENGTH⁽⁹⁾

Charging Conditions:

Electrolyte: 4 weight per cent H_2SO_4 in water
 Poison: 5 drops per liter of cathodic poison
 composed of 2 g phosphorus
 dissolved in 40 ml CS_2
 Current density: 10 ma/in.²

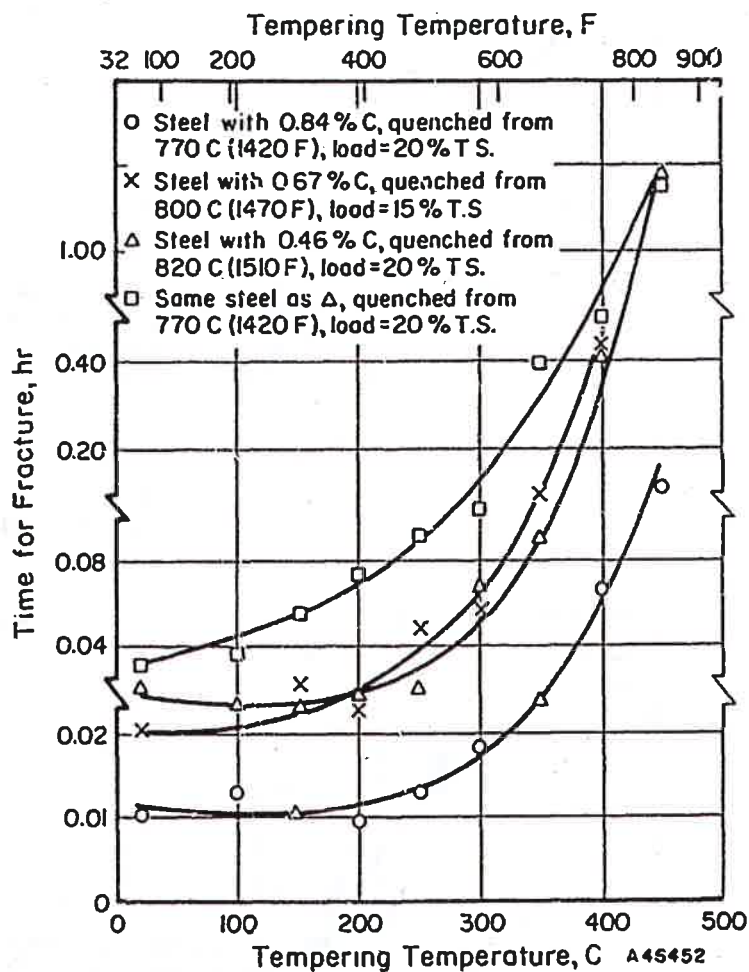


FIGURE 6. TIME FOR FRACTURE VS. TEMPERING TEMPERATURE FOR DIFFERENT CARBON STEELS CHARGED CATHODICALLY WITH HYDROGEN (AFTER GASIOR AND PRAJSNAR)⁽¹⁴⁾

Note the three breaks in the vertical time scale.

seven materials studied, the heat treatments used, and the resulting strength levels are listed in Tables 1 and 2. Both smooth (unnotched) and notched ($K_t = 2$ to 10) specimens were used. Hydrogen was introduced into the steel during cadmium electroplating at 200 ma/mm². By a suitable adjustment of the applied load, specimens of all seven steels including all strength levels examined could be made to fail, with a time delay, under sustained load as the result of hydrogen introduced by cadmium electroplating. Curves of applied stress versus time to failure were presented for each steel and each strength level studied, see Figure 8 for SAE 4340 as an example. From these curves, the rupture strength corresponding to a failure time of 100 hours was determined. This value has been plotted versus tensile strength for four of the steels in Figure 9. From their results, they concluded that the susceptibility of a steel to failure under sustained load after cadmium plating depends on the severity of the notch and on the metallurgical structure of the steel. They found that the silicon-modified steels studied were more resistant to hydrogen embrittlement at intermediate tempering temperatures than were the low-silicon steels. Also, the lower critical stress was higher for the high-silicon steels than for low-silicon steels for the intermediate tempering temperatures. An example of the general behavior of the silicon-rich steels is that exhibited by Hy-Tuf, shown in Figure 10. Although all the steels studied could be made to fail under sustained load after cadmium plating, two steels possessed relatively high resistance to delayed failure at strength levels as high as 270,000 psi when hydrogen was introduced in this manner. Hy-Tuf at a strength level of 230,000 psi showed only slight embrittlement under the cadmium-plating conditions used, as is shown in Figures 10 and 11. UHS-250 also was less sensitive to the embrittling action of electrodeposited hydrogen than were the low-silicon steels. Thus, these results suggest that steels with high silicon contents offer some advantage.

Srawley⁽²¹⁾ tested a wide variety of steels to obtain more extensive comparative data on the susceptibility to hydrogen embrittlement. He also tested a selection of non-ferrous alloys. The emphasis was on delayed fracture under constant sustained load. The specimens were severely cathodically charged with hydrogen (24 hours at 0.5 amp/in.²) so that even a slight degree of susceptibility to embrittlement of any of the alloys might be detected. The compositions and conditions of the materials used are given in Tables 3 and 4.

To compare a variety of materials, a convenient index of the susceptibility to hydrogen embrittlement is the ratio of the lower critical stress for failure to the notched tensile strength of the uncharged material. This ratio, which Srawley called the "static-fatigue ratio", will have a low value for materials that are highly susceptible to hydrogen-induced, delayed, brittle failure and will approach a value of 1.00 as the susceptibility becomes negligible. In Srawley's work, the small number of specimens available per material allowed only the determination of the limits between which the static-fatigue ratio should lie. The upper limit, called the failure-stress ratio, was defined as the ratio of the lowest nominal stress at which a specimen failed (within 100 hours) to the notched tensile strength of the uncharged material, the lower limit, called the survival-stress ratio, was defined as the ratio of the highest stress at which a specimen survived (for 100 hours or more) to the notched tensile strength of the uncharged material. These ratios are given in Table 5, along with the properties of the uncharged specimens and the time to failure of the specimen which failed at the lowest nominal stress, i. e., the time corresponding to the failure-stress ratio. In several cases, a specimen fractured while being loaded to the intended stress, so the remark "load increasing" is used in place of the time to failure. In six cases, specimens of relatively soft material which had survived 100 hours or more under load were found to

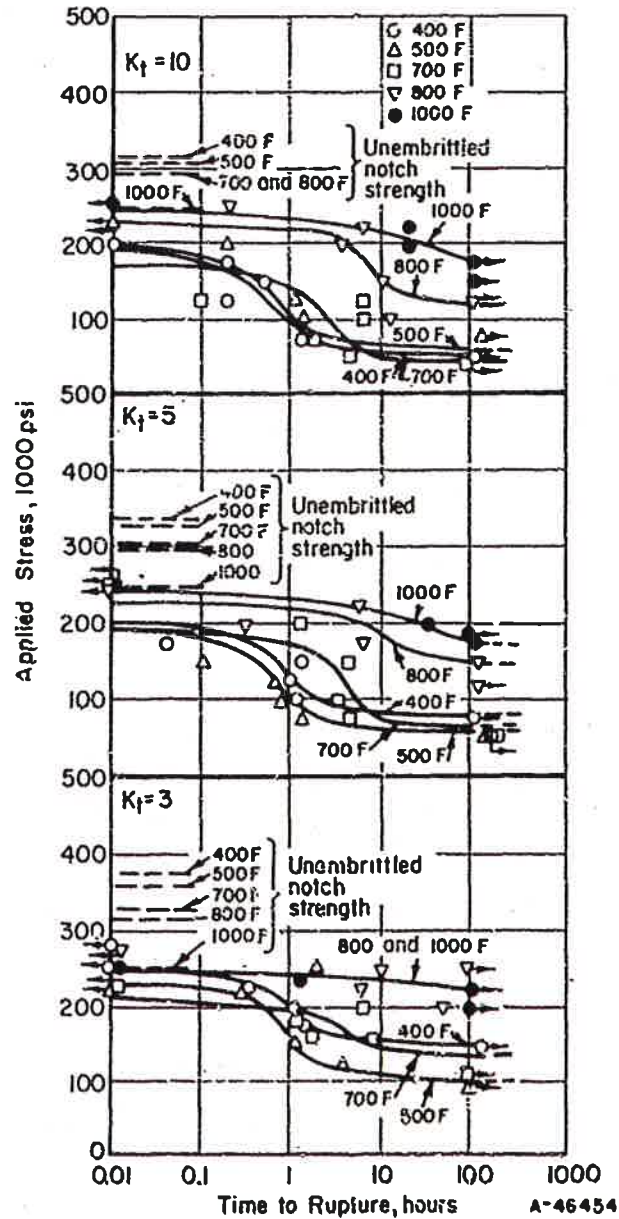


FIGURE 8. PLOTS OF APPLIED STRESS VERSUS TIME TO RUPTURE FOR CADMIUM-PLATED SAE 4340 STEEL TEMPERED AS INDICATED, FOR VARIOUS STRESS CONCENTRATIONS⁽¹⁹⁾

Austenitized at 1525 F, oil quenched.

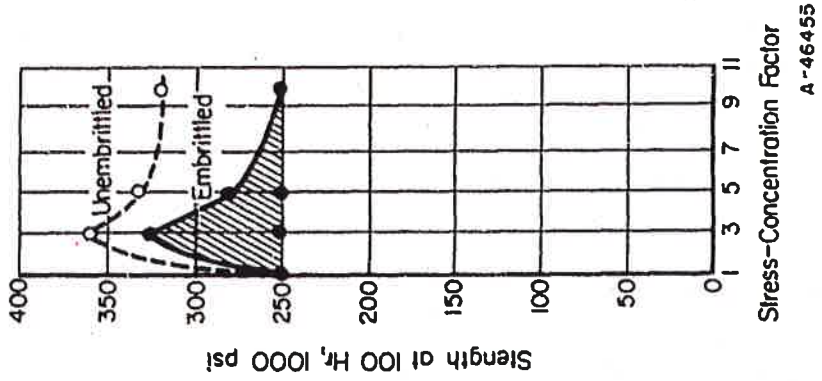


FIGURE 11. THE FRACTURE STRENGTH AT 100 HOURS VERSUS STRESS CONCENTRATION FOR CADMIUM-PLATED HY-TUF STEEL TEMPERED AT 700 F(19)

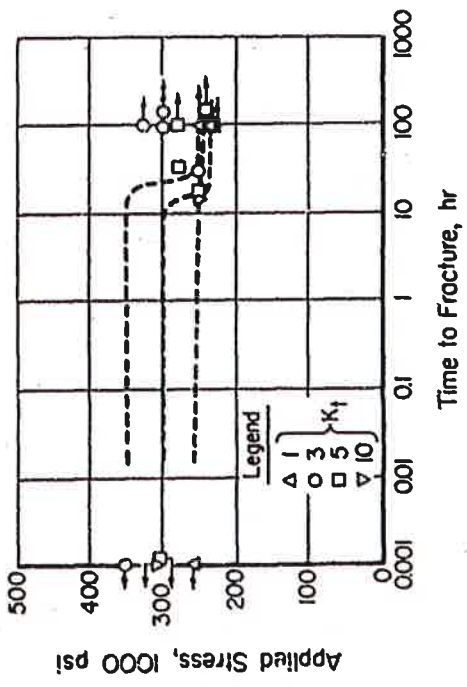


FIGURE 10. PLOT OF STRESS VERSUS TIME TO FRACTURE AT INDICATED STRESS CONCENTRATION FOR CADMIUM-PLATED HY-TUF STEEL TEMPERED AT 700 F(19)

K_t = stress-concentration factor of the notch. Austenitized for 2 hours at 1575 F, oil quenched, and tempered at 700 F.

TABLE 4. CONDITIONS OF MATERIALS TESTED IN A COMPARATIVE STUDY OF SUSCEPTIBILITY TO DELAYED, BRITTLE FAILURE⁽²¹⁾

Material	Condition
AISI 52100 steel	Oil quenched from 1550 F (1/2 hr), then tempered as indicated ^(a)
AISI 4340 steel	Oil quenched from 1550 F (1/2 hr), then tempered as indicated ^(a)
AISI 4130 steel	Oil quenched from 1550 F (1/2 hr), then tempered as indicated ^(a)
AISI 1020 steel	Water quenched from 1650 F (1/2 hr), then tempered as indicated ^(a)
Armco iron	Annealed (as received)
Malleable cast iron	Oil quenched from 1500 F (20 min), then tempered at 500 F for 3 hr and water quenched
AISI 422 steel (modified)	Oil quenched from 1850 F (1/2 hr), then tempered as indicated ^(a)
PH Steel W	Received in solution-treated condition, then aged 2 hr at 950 F and air cooled
PH Steel A	Received in solution-annealed condition
RH950	Air cooled from 1750 F (1/2 hr), refrigerated for 16 hr at -100 F, aged at 950 F for 1 hr and air cooled
TH1050	Air cooled from 1450 F (1-1/2 hr), aged 1050 F for 1-1/2 hr and air cooled
PH Steel B	Received in solution-annealed condition
H875	Air cooled from 875 F (1 hr)
Austenitic Steel T	Cold rolled to 30 per cent reduction of area after forging and water quenching from 2000 F (1/2 hr)
AISI 410 Steel	Oil quenched from 1700 F (1 hr), then tempered as indicated ^(a)
AISI 304 Steel	Cold rolled to 46 per cent reduction of area
K Monel	As received (hot rolled)
Monel	As received (hot rolled)
Inconel	As received (hot rolled)
Copper Beryllium No. 25	Received in solution-annealed condition, aged at 600 F for 18 hr and air cooled
Bronze	As received (hot rolled)
Manganese bronze	As received
Aluminum bronze	As received
Beta brass	Air cooled from 1000 F (2 hr) after hot forging to size
7075 aluminum alloy	As received (stress relieved and aged)

(a) See Table 5.

TABLE 5. (Continued)

Material	Condition ^(a)	Uncharged Properties				Hydrogen-Charged Specimens			
		Rockwell Hardness Number	Ultimate Tensile Strength, 1000 psi	Notched Tensile Strength, 1000 psi	NTS UTS	Number of Specimens Tested	Survival- Stress Ratio, 100 hr	Failure- Stress Ratio, minimum	Time to Failure
AlSI 304 steel	46% cold rolled	C-28	131.0	203.0	1.55	5	1.00	1.00	Load increasing ^(c)
K Monel	As rec'd.	C-28.5	139.0	220.0	1.58	4	0.93 ^(b)	0.98	Load increasing ^(c)
Monel	As rec'd.	C-24.5	116.0	185.0	1.59	6	0.86 ^(b)	0.95	Load increasing ^(c)
Inconel	As rec'd.	B-72	88.3	115.0	1.31	3	0.79 ^(b)	0.99	Load increasing ^(c)
Copper Beryllium No. 25	600/18	C-41	(185.0)	130.0	(0.70)	4	0.97	1.02	Load increasing ^(c)
Bronze	As rec'd.	B-92	--	135.5	--	4	0.95	1.00	Load increasing ^(c)
Manganese Bronze	As rec'd.	B-96	131.0	156.0	1.19	4	0.90	0.95	49 hr
Aluminum Bronze	As rec'd.	B-81	83.4	106.0	1.27	4	0.95	1.00	Load increasing ^(c)
Beta brass	1000/2	E-84	60.0	75.6	1.26	4	0.61	0.66	20 hr ^(d)
7075 aluminum alloy	As rec'd. (aged)	B-88	80.0	101.5	1.27	4	0.97	1.02	Load increasing ^(c)

(a) The values given are for tempering temperature and time; for instance, T600/1 indicates that a material was tempered for 1 hour at 600 F after the hardening treatment given in Table 4.

(b) Crack detected at notch root after unloading, although load had been sustained for at least 100 hours without fracture.

(c) Lowest stress for fracture was that obtained in the continuous-loading notched tensile test of the charged material.

(d) Delayed fracture of specimens not charged with hydrogen also occurred.

A study of delayed cracking of steel weldments was performed by Beachum, Johnson, and Stout⁽²⁴⁾. They studied the effects of hydrogen, stress (restraint), and steel composition. Steels studied included AISI 1020 and ASTM A212 plain-carbon steels, and HY-80 and AISI 4140 alloy steels. Delayed cracks were produced in weldments of all four steels.

Schuetz and Robertson⁽²⁵⁾ studied the delayed failure of a series of plain-carbon steels and a series of four nickel steels that contained from 5 to 30 per cent nickel. Hydrogen was introduced into the steels by exposure to H₂S solution and by cathodic charging. With either method of introducing hydrogen, delayed failures were obtained in the steels in the ferritic or martensitic condition. However, no failure was obtained with the 30 per cent nickel steel when it was treated so as to be fully austenitic at room temperature.

Other investigators have verified that martensitic stainless steels also are subject to hydrogen embrittlement and delayed, brittle failure. Uhlig⁽²⁶⁾ has described the hydrogen embrittlement of a 13 per cent chromium stainless steel, and Lillys and Nehrenberg⁽²⁷⁾ reported on embrittlement of Types 410, 420, and 422 stainless steel.

A few of the other steels reported to be embrittled by hydrogen include SAE 1000⁽²⁸⁾, SAE 1050 spheroidized-annealed strip⁽²⁹⁾, SAE 6150⁽³⁰⁾, clock-spring steel⁽³¹⁾, and SAE 4140 cold-drawn wire with a tensile strength of 170,000 psi⁽¹⁰⁾.

Blanchard and Troiano⁽³⁾ performed an investigation to determine whether the hydrogen embrittlement of nickel is of the same nature as that of steel and to determine the effect of alloying on the magnitude of the embrittlement in nickel. The study included 25Cr-20Ni austenitic stainless steel. The materials studied were as follows:

	Composition, per cent		
	Ni	Cr	Fe
"A" Nickel	99.4		0.15
72Ni-28Fe	72.7		27.2
51Ni-49Fe	51		49
Nilvar	36		64
Nichrome I	60	16	24
Nichrome V	80	20	
25-20 stainless steel	19.7	24.9	52.8

Both thermal and cathodic charging were used to introduce hydrogen into the alloys. Thermal charging was used for the 25-20 stainless steel in which the diffusion rate of hydrogen is low at room temperature, the other alloys were charged cathodically. The authors found that the nickel and some of the nickel-base alloys were embrittled by hydrogen when charged for several hours at a high current density. Studies of the strain-rate dependence and the temperature dependence of the embrittlement, and of the recovery of ductility upon aging, showed that this embrittlement was of the same type as that of ferritic and martensitic steels.

The embrittlement was a maximum for pure nickel and nil for the 51Ni-49Fe alloy, Nilvar, and 25-20 stainless steel. The variation in susceptibility toward hydrogen embrittlement of Ni-Cr-Fe alloys is shown in Figure 12. An apparent anomaly is the observation that the hydrogen embrittlement of a nickel-iron alloy decreased with

fully austenitic condition, but Blanchard and Troiano^(37, 3) did find embrittlement of nickel and certain nickel-base austenitic materials under severe charging conditions. Austenitic materials that are resistant to hydrogen embrittlement become susceptible when treated so as to partially transform to body-centered cubic structures, as Jones⁽³⁸⁾ found when chemical milling Type 301 stainless steel that had been cold worked to a high strength level.

EFFECT OF STRENGTH LEVEL

Many experiments have shown that both the minimum stress and the time required to produce delayed, brittle failure by hydrogen decrease as the nominal tensile strength of the steel is increased. On the basis of these experiments alone, delayed-type brittle failures would be expected to be an increasingly severe problem as the strength level of steel is increased. Because of the ever-increasing demand for materials of higher and higher strength in the aircraft and missile industries, for weight savings, this general behavior made an understanding of the nature of hydrogen-induced, delayed, brittle failure of steel imperative. The results of some of these experiments that show the effect of strength level on the phenomenon are considered in this section.

Slaughter et al.⁽⁸⁾ studied the effect of strength level with a group of SAE 4340 steel specimens in which the ultimate tensile strength was varied from approximately 300,000 psi to 142,000 psi. All of these specimens were fully quenched to produce martensitic structures, and then tempered at temperatures in the range from 300 to 1200 F to produce the desired variations in strength. Smooth (unnotched) specimens were continuously charged with hydrogen cathodically while under sustained load. The results are shown in Figures 2 (page 6) and 13. In addition, Figure 13 shows the effect of differences in structure, but this subject will be discussed later. As the strength level was decreased from 300,000 psi to 142,000 psi, the time to rupture in the higher range of stress increased by a factor of approximately 100; the stress required to cause rupture in 10,000 minutes increased from 15,000 to 45,000 psi as the strength level was decreased in that range (see Figure 2).

Although it is unlikely that the conditions of these tests would be encountered in service, the results obtained show that hydrogen entering the steel while it is under stress can cause it to lose more than 90 per cent of its ability to withstand a sustained load, in the case of steel heat treated to a high strength level. Even at the lowest strength level tested for the tempered martensite (142,000 psi), the steel lost approximately two-thirds of its load-carrying ability. In these experiments, rupture occurred in a tempered-martensite structure having a tensile strength as low as 142,000 psi. However, service failures nearly always have been restricted to steels having a higher strength level. This was attributed to the fact that in these experiments the specimens contained more hydrogen than would be expected in service.

The same steel was isothermally transformed at 1200 F to produce a pearlitic structure which had a tensile strength of 75,000 psi. Under the same charging and test conditions, delayed failures were obtained in unnotched specimens at this strength level, as indicated by the following tabulation and by the appropriate curve in Figure 2 (page 6).

<u>Applied Stress, psi</u>	<u>Time to Rupture, minutes</u>
75,000	516
71,000	630
70,000	978
64,000	1872
50,000	Did not fail in 13,242 min (221 hr)
50,000	Did not fail in 14,334 min (239 hr)

Frohberg, Barnett, and Troiano⁽⁵⁾ at Case Institute of Technology studied the effect of strength level of SAE 4340 steel by using sharp-notched specimens cathodically precharged with hydrogen. Sharp notches were used to localize the region of fracture and to provide a multiaxial stress state. The results obtained are shown in Figure 1 (page 5). With their conditions, applied stresses as low as 40 per cent of the yield strength caused failure in a matter of only a few hours. Identical notched specimens in the uncharged condition were stressed at high loads, as indicated in the figure, and remained unbroken after times of more than 250 hours. Regardless of the strength level, the time to failure was always of the same order of magnitude (approximately 1 to 8 hours).^{*} For a given strength level, there appeared to be only a slight dependence of failure time on the applied stress. Thus, they found that the delay in time for failure was evidently independent of strength level and only slightly dependent upon applied stress for the particular test conditions used. Material at the highest strength level exhibited a lower value of the upper critical stress than did material at the other two strength levels. Barnett and Troiano^(39, 6) showed the effect of the same cathodic charging conditions on the mechanical properties of both smooth and notched specimens of this steel heat treated to three strength levels. The results are shown in Table 6. For the 240,000-psi strength level, the lower critical stress was 75,000 psi. In studying 12 heats of SAE-AISI 4340 steel, the Case research workers⁽¹⁵⁾ found that the lower critical stress was independent of the strength level for their test conditions, but the charged notched tensile strength tended to be inversely related to the strength level, at least at the higher strengths.

Figure 14 shows the results Rinebolt⁽¹²⁾ obtained for tensile tests of AISI 4340 steel heat treated to three different strength levels and cathodically charged for various times. These comparisons are based on per cent of original tensile strength. The data show that 60 per cent of the tensile strength was lost by a steel of 209,000-psi tensile strength (uncharged specimen) after charging for 4 hours under the conditions used. The same loss in tensile strength was obtained for the steel heat treated to the 287,000-psi strength level after only 1/2 hour of charging. Table 7 presents the actual values obtained. Note that for many charging conditions the material that was the strongest in the uncharged condition became the weakest. Also, note that the reduction in area and elongation decreased to less than 1 per cent after charging for only 5 minutes for all strength levels investigated.

Sachs and co-workers at Syracuse University⁽¹⁹⁾ studied the effect of strength level on delayed failures for several materials when the hydrogen was introduced

^{*}These results seem to be somewhat contrary to those obtained by Slaughter et al.⁽⁶⁾. Much of the difference is probably the result of differences in test procedure in the two investigations. Slaughter and co-workers used unnotched specimens that were cathodically charged continuously while under sustained stress, while the Case Institute investigators used notched specimens that were precharged with hydrogen and were not charged during the time they were under the sustained stress. It will be shown later that such differences in stress concentration and in the amount and distribution of hydrogen in the test specimen do affect the initiation and propagation of brittle fracture.

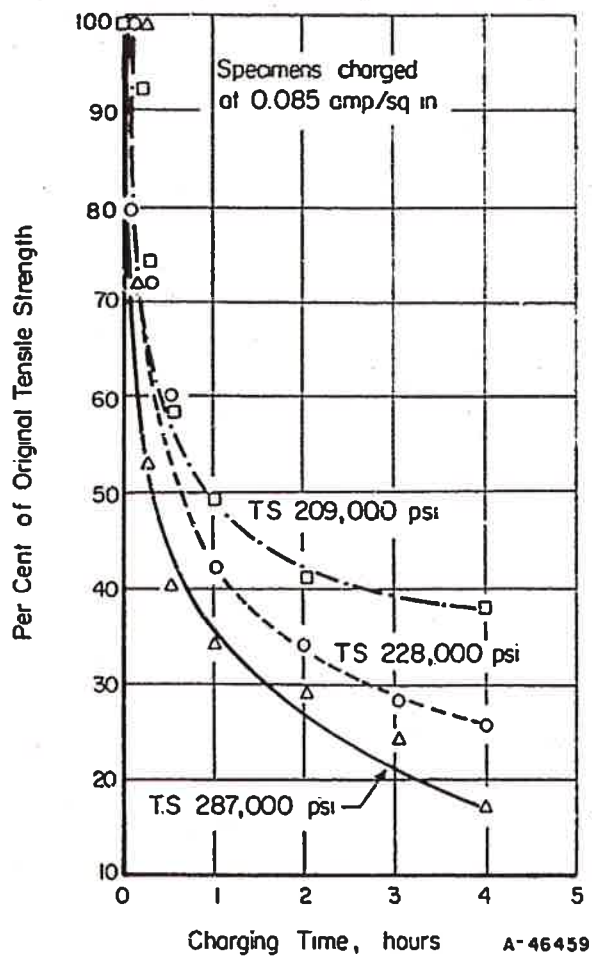


FIGURE 14. EFFECT OF HYDROGEN CHARGING ON TENSILE PROPERTIES FOR AIR-MELTED STEEL AT THREE STRENGTH LEVELS(12)

AISI 4340 steel.

the tempering temperature was raised from 700 F. Even after tempering at 1000 F (165,000-psi ultimate tensile strength), delayed failures occurred as the result of hydrogen electrodeposited during cadmium plating. Figure 15 shows the change in "minimum fracture stress", taken as the fracture stress corresponding to a rupture time of 100 hours, with change in tempering temperature (change in strength level). The minimum stress was raised considerably by tempering at the higher temperatures (800 to 1000 F). By comparing these data with the data for smooth specimens ($K_t = 1$) in Figure 16, it is seen that the curve of breaking stress at 100 hours versus tempering temperature for cadmium-plated smooth specimens in Figure 15 differs little from that measured for unembrittled smooth specimens. Although sustained-load failures occurred with a delay for smooth specimens in which the hydrogen was introduced only by commercial cadmium electroplating (Figure 16), such failures took place with little drop in stress.

Data for 98B40 steel tempered at various temperatures are shown in Figures 17 and 18. These data are rather similar to those obtained for SAE 4340 steel. Similar results also were obtained for the vanadium-modified SAE 4330 steel (see Figure 19).

Valentine⁽²⁸⁾ studied the delayed failure of zinc-plated lockwashers made from SAE 1060 wire. Acid pickling was used prior to plating. The lockwashers were tested by placing them between case-hardened flat washers on a bolt and drawing them down flat with a nut, they were examined periodically for failures while clamped on the bolts. This investigator found a strong dependence of the tendency towards delayed failure on strength level, the lower the hardness (strength), the smaller the percentage of failures encountered. Some of his results that show the effect of strength level (in terms of hardness) are given in Table 8. Stefanides⁽²⁹⁾ studied the delayed failure of electroplated dome lockwashers fabricated from SAE 1050 steel strip; these were acid descaled and cadmium plated after hardening. Upon loading to a fixed load for a week, he, too, found that the percentage of failures was directly related to the hardness.

TABLE 8. RESULTS OF TESTS MADE ON HEAVY LOCKWASHERS ELECTROPLATED WITH ZINC^(a)(28)

Treatment After Plating	Rockwell C Hardness	Number Tested	Number Broken After 1 Week	Per Cent Broken
None	62	200	200	100
None	55	200	184	90
None	50	200	74	37
None	47	200	31	15
None	42	200	0	0
Heated at 400 F for 4 hours	52	200	17	8
Heated at 400 F for 4 hours	50	200	0	0
Heated at 400 F for 4 hours	47	200	0	0
Heated at 400 F for 4 hours	42	200	0	0

(a) 7/16-inch heavy lockwashers plated with 0.0002 inch of zinc plate.

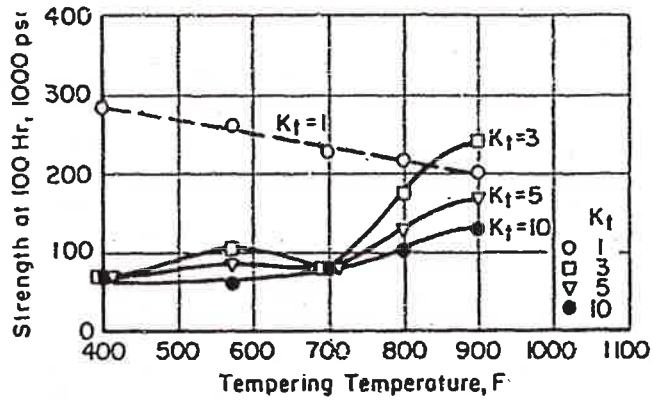


FIGURE 17. THE FRACTURE STRENGTH AT 100 HR VERSUS TEMPERING TEMPERATURE WITH STRESS CONCENTRATION AS PARAMETER FOR CADMIUM-PLATED 98B46 STEEL (1)

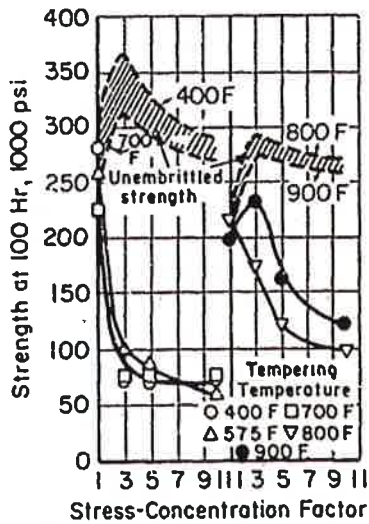
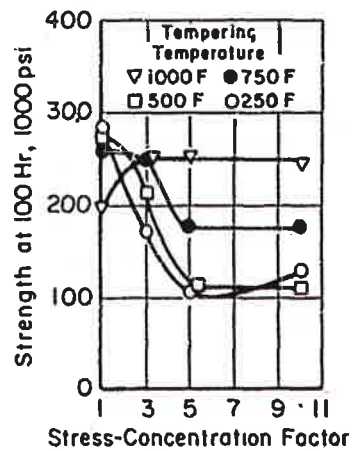


FIGURE 18. THE FRACTURE STRENGTH AT 100 HR VERSUS STRESS CONCENTRATION WITH TEMPERING TEMPERATURE AS PARAMETER FOR CADMIUM-PLATED 98B46 STEEL (19)



A 46461

FIGURE 19. THE FRACTURE STRENGTH AT 100 HR VERSUS STRESS CONCENTRATION WITH TEMPERING TEMPERATURE AS PARAMETER FOR CADMIUM-PLATED 4330 VANADIUM-MODIFIED STEEL (19)

critical value of applied stress below which delayed failure did not occur in material of a given strength level. The test generally was discontinued if a specimen remained unbroken after sustaining the static load for 100 hours, but times as long as 2100 hours without failure were observed. For the specimen geometry, notch acuity, charging conditions, and test conditions used in these experiments, the lower critical stress was nearly the same for the three strength levels (270,000 psi, 230,000 psi, and 200,000 psi). However, this is not always the case for other conditions.

These investigators clearly demonstrated the necessity for exceeding some critical stress value to produce delayed failure, by an experiment in which they varied the notch acuity of the test specimen. The results of this experiment are shown in Figure 20. For the sharp notch (with the highest degree of stress concentration), the smallest load served to produce delayed failure. A greater applied stress was required for failure to occur in the specimens with the milder, 1/32-inch-radius notch. For the specimens with a notch root radius of 2 inches, the stress concentration resulting from the notch was very slight, and the lower critical stress for delayed failure was no more than 5,000 psi below the value of the notched tensile strength of charged specimens. Thus, for these precharged specimens, the lower critical stress was raised markedly as the notch acuity was decreased.

In another experiment, these same workers showed that the lower critical stress is not constant for this type of specimen. Two series of specimens that came from the same bar of steel but which were prepared separately gave the results shown in Figure 21. Despite all the precautions to maintain uniformity between batches, some factor was different. The specimens from which the lower curve was obtained may have had a more severe concentration of residual stress than the specimens from which the upper curve was obtained. In other words, the one set of specimens was, in essence, preloaded and required a smaller applied load to give delayed failure.

In a continuation of this work, Barnett and Troiano⁽³⁹⁾ used the resistance method of crack-propagation measurement to evaluate the effect of applied stress, as well as certain other variables, on delayed, brittle failure. These studies were made with precharged, notched specimens of SAE 4340 steel at the 230,000-psi strength level. Charging conditions were the same as for the work just described. The delayed-failure characteristics for these conditions are illustrated in Figure 22. The increase in electrical resistance was measured as a function of time during static loading at various stresses within the range of 100,000 to 200,000 psi; the results are shown in Figure 23. With the data in Figure 23 and by referring to resistance calibration curves, they obtained crack-area data as a function of time for the indicated applied stresses. Crack area was expressed as a percentage of the area under the notch. These data are shown in Figure 24. In Figure 25, the crack-propagation curves are shown in terms of the alternative parameter, radial crack depth. These figures show that, for the test conditions used, there was little or no incubation time for crack initiation (the minimum time required for a reliable resistance measurement was 30 seconds after application of the load). Immediately upon loading above the lower critical stress, the material was damaged permanently, that is, a crack had been initiated. The extent of damage depended on time and the applied stress. Thus, the magnitude of the applied load influenced the crack-growth behavior. The extent of rapid crack growth incurred in the first stage of the fracture process was, in general, greater the less the magnitude of the applied load. The conditions existing at the end of the third stage, that is at fracture, are summarized in Table 9. The applied stress had no significant effect on the delayed-failure fracture stress, which was slightly higher than the notch-tensile strength of the uncharged base material in every instance.

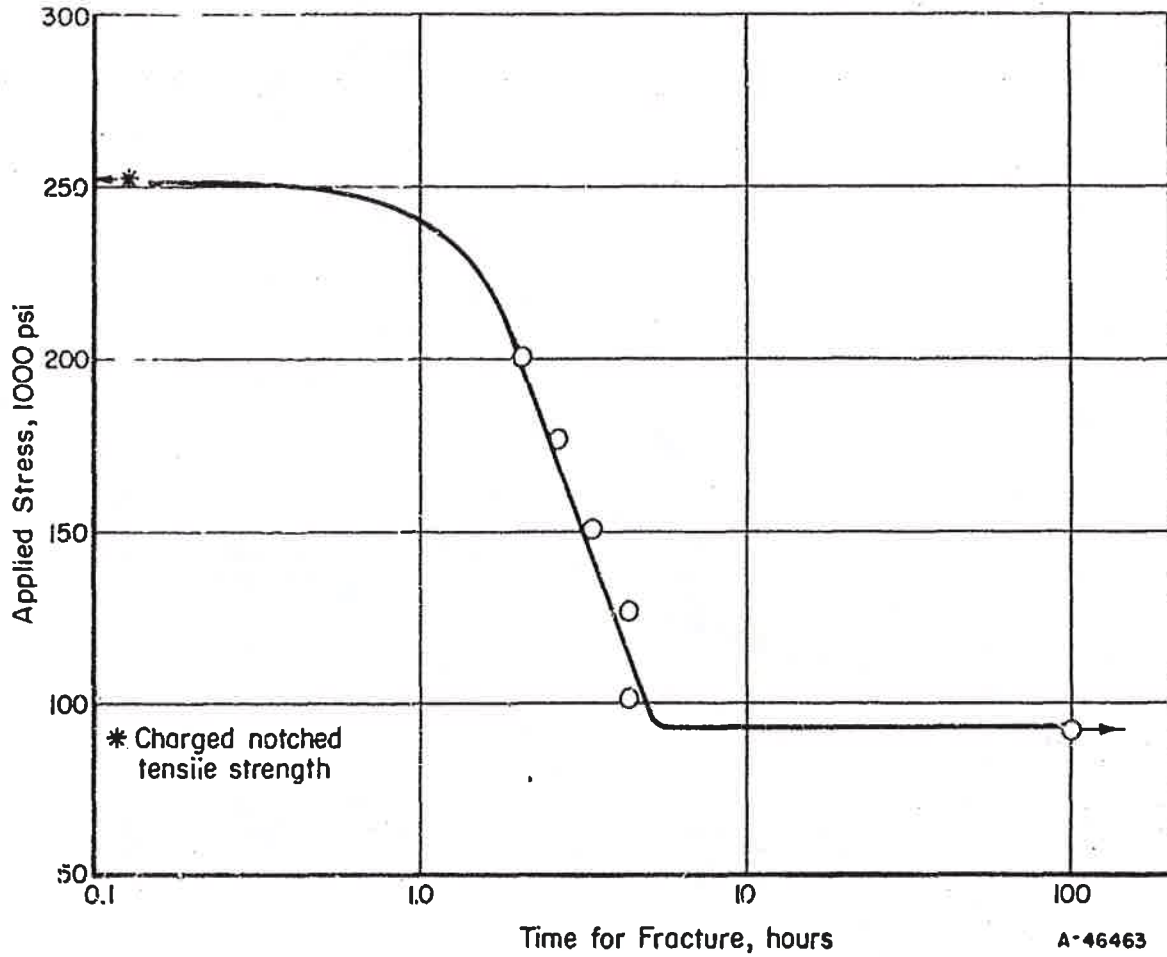
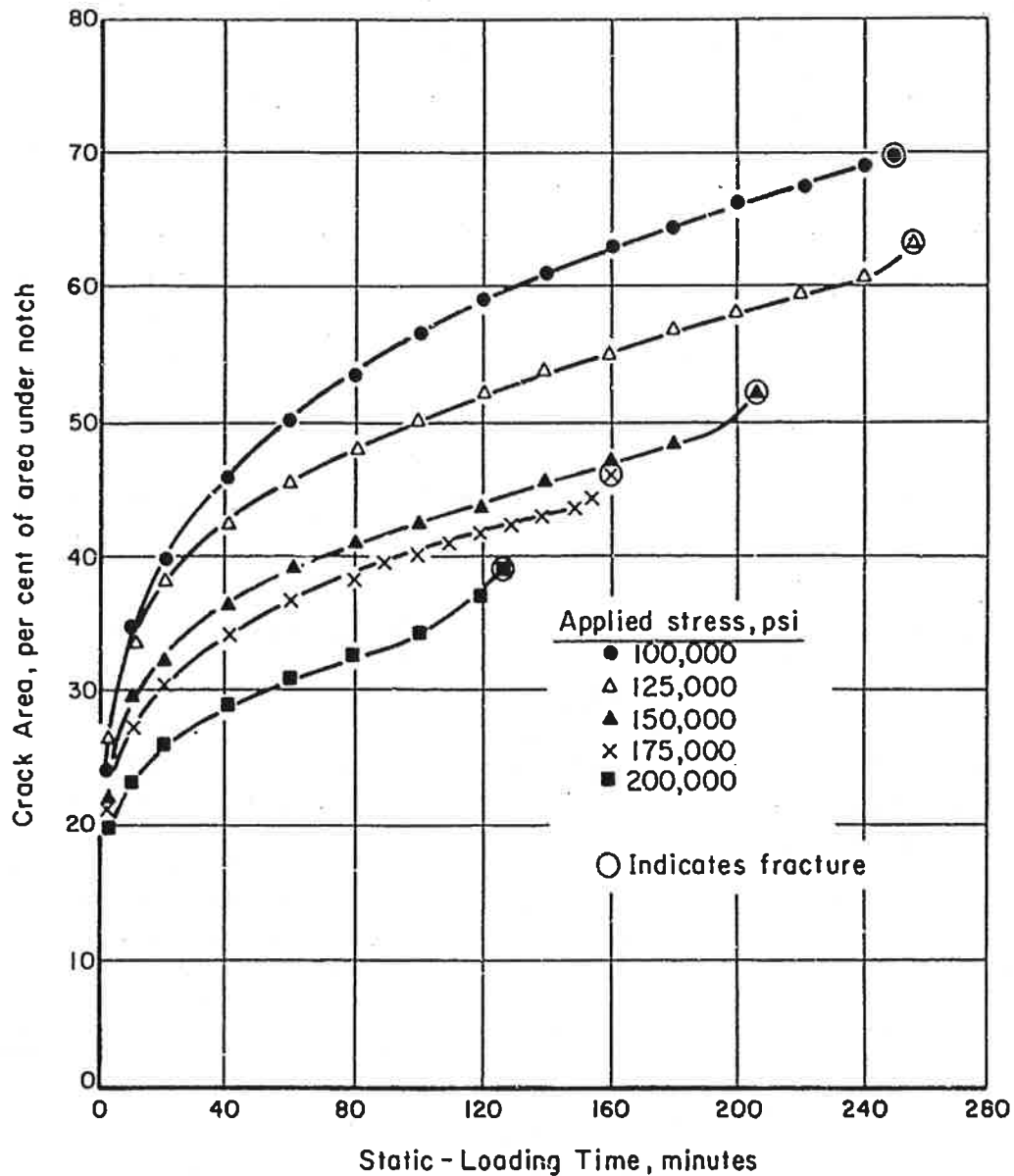


FIGURE 22. DELAYED-FAILURE BEHAVIOR OF SHARP-NOTCH SPECIMENS OF SAE 4340 STEEL AT THE 230,000-PSI STRENGTH LEVEL⁽³⁹⁾

Aged 5 minutes. Case Institute of Technology Charging Condition A, as given in Figure 20.



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FIGURE 24. EFFECT OF APPLIED STRESS ON CRACK PROPAGATION WITHIN THE DELAYED-FAILURE RANGE OF SHARPLY NOTCHED SPECIMENS OF SAE 4340 STEEL AT THE 230,000-PSI STRENGTH LEVEL(39)

Aged 5 minutes. Case Institute of Technology Charging Condition A, as given in Figure 20.

TABLE 9. EFFECT OF APPLIED STRESS ON THE DELAYED-BRITTLE-FAILURE BEHAVIOR OF SAE 4340 STEEL, AT THE 230,000-PSI STRENGTH LEVEL⁽³⁹⁾

Static Applied Stress, psi	Fracture Time, minutes	Crack Area, per cent of area under notch	Radial Crack Depth, 10 ⁻³ inch	Delayed-Failure Fracture Stress, psi	Surface Energy (S), 10 ⁷ ergs/cm ²
100,000	253	70.5	48.0	339,000	4.00
125,000	256	63.5	41.5	343,000	4.60
150,000	207	52.5	32.5	316,000	4.44
175,000	160	45.5	27.5	321,000	4.93
200,000	127	39.0	23.0	328,000	5.40

Note: Case Institute of Technology Charging Condition A, as given in Figure 20.
Aged 5 minutes at room temperature after charging.

The effect of applied stress when smooth specimens were cathodically charged continuously while under static load was demonstrated by the results of Elsea and co-workers at Battelle Institute⁽⁸⁾. Variations in applied stress affected the time to rupture in a similar manner under a wide range of strength levels, compositions, structures, and, to a certain extent, hydrogen contents. When other conditions were held constant, there were two ranges of stress which produced different effects on the time to rupture, as is shown in Figure 2 (page 6). In the higher range of applied stress, the time to rupture was relatively short and was only moderately affected by a change of stress. For example, as the stress was increased from 60,000 psi to 180,000 psi, the time to rupture decreased only from 20 minutes to 6 minutes for a steel heat treated to 230,000-psi ultimate tensile strength and charged under the standardized conditions adopted. These investigators recognized that, in those specimens which failed after a relatively short time, the time to rupture probably was controlled more by the depth of hydrogen penetration than by the failure mechanism. In the lower range of stress, the time to rupture was longer by as much as a factor of 100. Time to rupture was greatly influenced by stress in this range, a slight decrease of stress resulted in a large increase in the time to rupture. For the conditions of the previous example, decreasing the applied stress from 40,000 psi to 25,000 psi increased the rupture time from 40 minutes to approximately 10,000 minutes.

To be certain that the action of the electrolyte at the specimen surface was not influencing the failures in the delayed-failure tests described above, the Battelle investigators performed another series of experiments. In these experiments, specimens were statically loaded in bending and charged cathodically on the compression side, thus eliminating any surface effect of the electrolyte on the side stressed in tension. The specimens used in this series of experiments were bars of SAE 4340 steel 1/2 by 1-1/2 by 8 inches, all heat treated to an ultimate tensile strength of approximately 230,000 psi. An electrolytic cell was cemented to one side of each specimen, with a portion of that side exposed as the cathode. A static bending moment was applied to the specimen so that the side to which the cell was attached was stressed in compression and the side exposed to the atmosphere was stressed in tension. The tension surfaces of the specimens were notched with 0.020-inch-wide transverse slots of varying depth. The stress

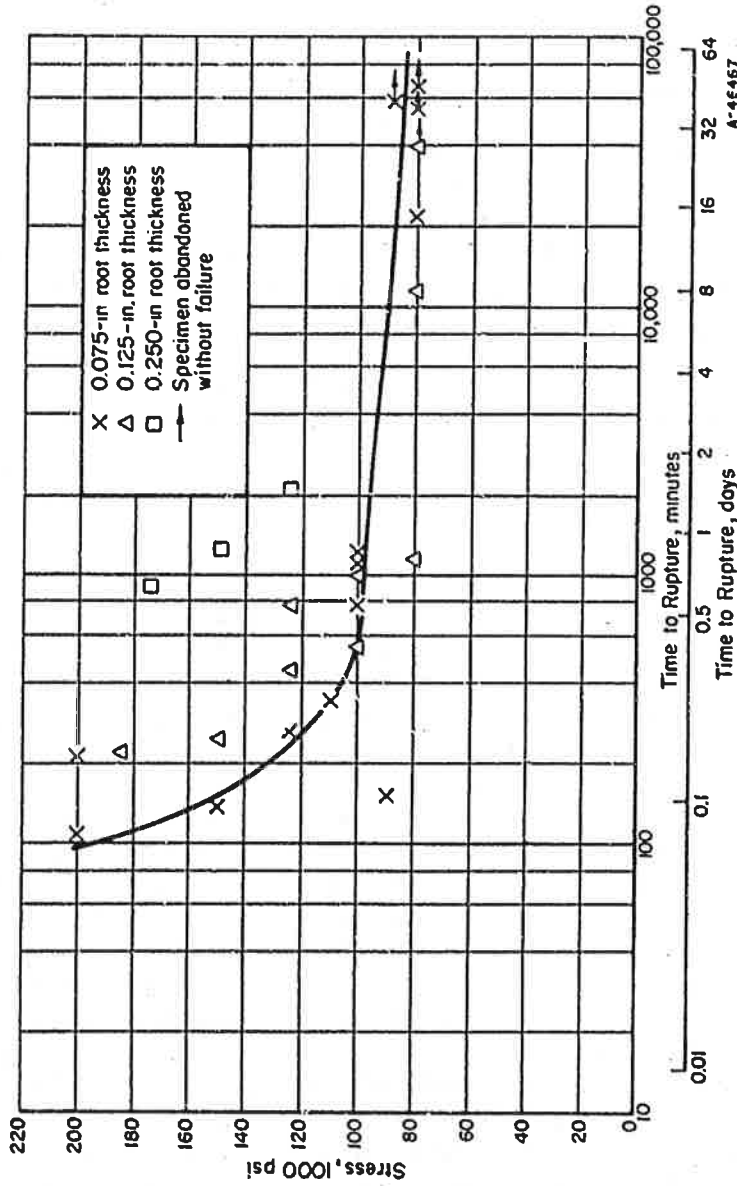


FIGURE 26. DELAYED-BRITTLE-FAILURE CHARACTERISTICS OF NOTCHED SPECIMENS OF AN SAE 4340 STEEL, LOADED IN BENDING WHILE BEING CHARGED CATHODICALLY WITH HYDROGEN IN A SULFURIC ACID ELECTROLYTE ON THE COMPRESSION SIDE(8)

The specimens were heat treated to a tensile strength of 230,000 psi.

Charging Conditions:

- Electrolyte: 4 weight per cent H₂SO₄ in water
- Poison: 5 drops per liter of cathodic poison composed of
2 g phosphorus dissolved in 40 ml CS₂
- Current density: 33 ma/in.².

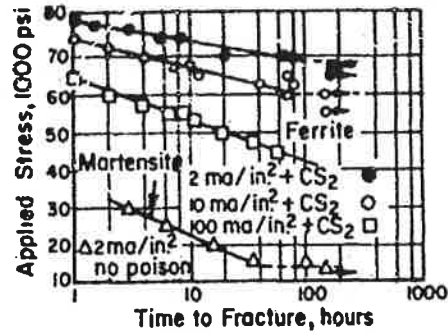


FIGURE 27. DELAYED FRACTURE OF FERRITE AND MARTENSITE IN AN IRON-NICKEL ALLOY (10Ni-90Fe) UNDER CONSTANT APPLIED STRESS AND CONSTANT HYDROGEN (SATURATION) CONCENTRATION⁽²⁵⁾

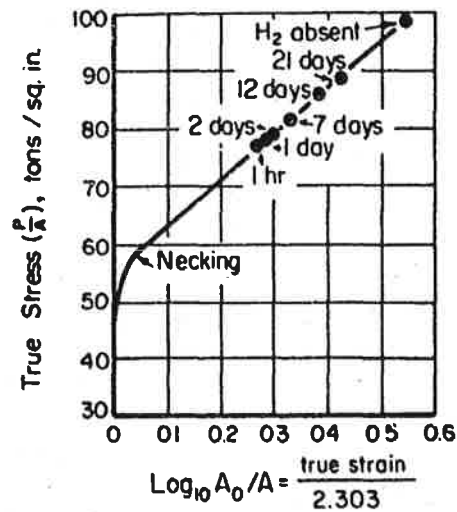


FIGURE 28. TRUE STRESS-TRUE STRAIN CURVES FOR A HYDROGEN-IMPREGNATED 3Cr-Mo STEEL AFTER STANDING IN AIR FOR VARYING PERIODS⁽⁴²⁾

P = load

A_0 = original cross-sectional area

A = instantaneous cross-sectional area at load P.

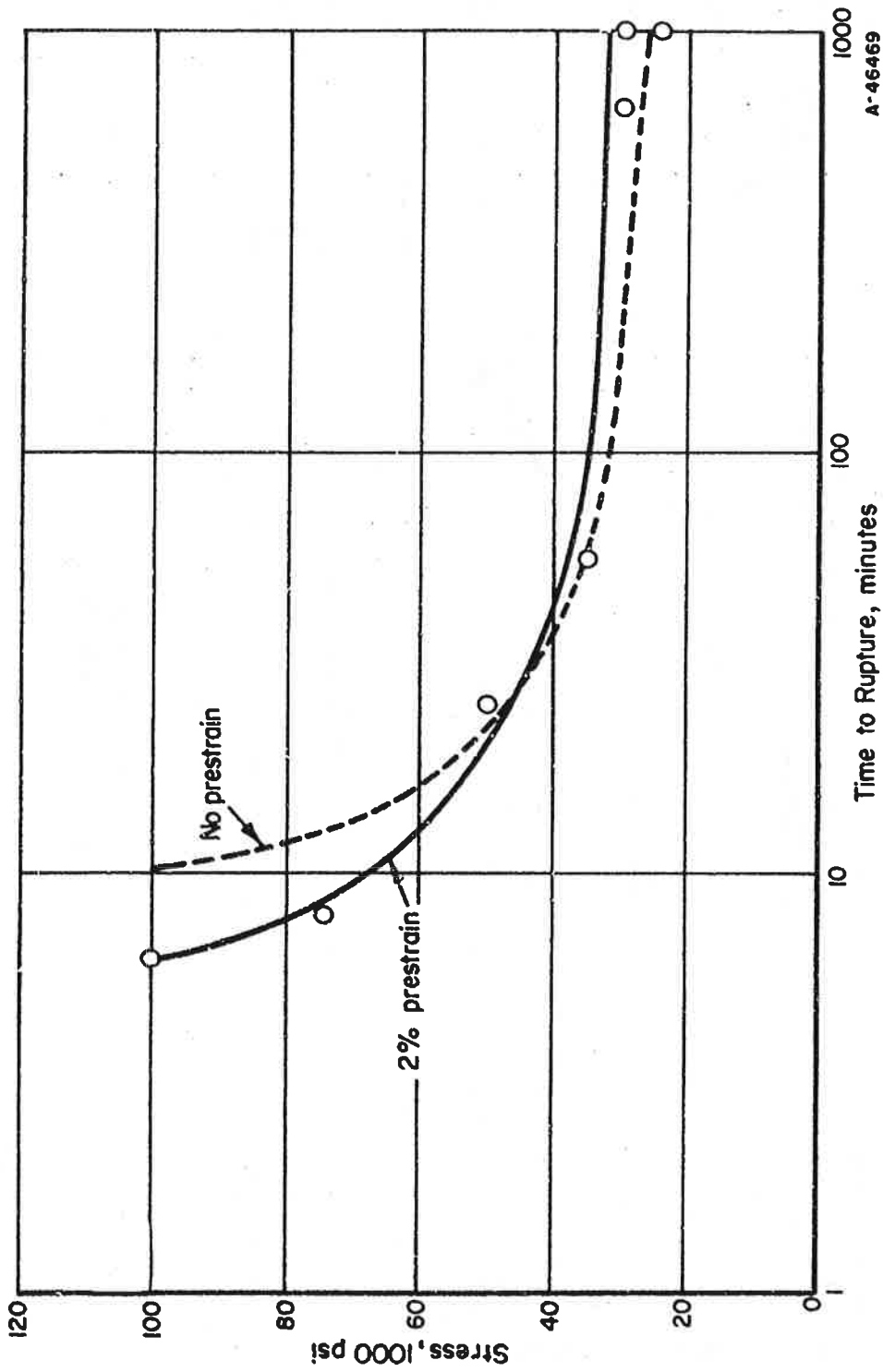


FIGURE 29. TIME FOR FAILURE AS A FUNCTION OF APPLIED STRESS WITH AND WITHOUT 2 PER CENT PLASTIC PRESTRAIN(9)

SAE 4340 steel, ultimate tensile strength 230,000 psi.

Charging Conditions Used:

Electrolyte: 4 per cent by weight of H_2SO_4 in water

Poison: 5 drops per liter of cathodic poison composed of
2 g phosphorus dissolved in 40 ml CS_2

Current density: 10 ma/in.².

hydrogen outgassing. The difference in shape of the two aging curves resulted only from the strain and not from immersion in liquid nitrogen. This was shown by specimens that were treated identically except that, for the one group, no straining was done during the immersion in liquid nitrogen. Specimens of the latter group exhibited ductilities that fell on the aging curve for unstrained specimens.

These investigators used these data to evaluate proposed theories of hydrogen embrittlement. They considered that, prior to straining, a steady-state distribution exists between hydrogen in the lattice and hydrogen in the voids. Straining changes the steady-state distribution by increasing the occlusive capacity of the voids. Thus, establishment of a new steady-state distribution requires hydrogen to move from the lattice to the voids. During straining at -321 F, hydrogen is immobile, however, at 150 F the hydrogen diffusion rate is vastly increased, and hydrogen will diffuse to the voids during the aging treatment. These workers discussed both the pressure theory and the classical adsorption theory and showed that both required increasing embrittlement during initial aging. Since this requirement was at variance with the experimental results shown in Figure 30, they concluded that neither mechanism was satisfactory. Therefore, they developed a new theory which is discussed later. However, according to their hypothesis, the strain magnitude influences the aging characteristics. As the strain is increased, the steady-state hydrogen content of the voids will increase, and the lattice hydrogen content must decrease.

Other experiments showed that the pseudorecovery observed in the first stage of aging is accelerated by increasing strain, which is in agreement with the postulated mechanism. This behavior is shown by the aging curves for hydrogenated specimens strained 3 per cent or 6 per cent at -321 F and aged at 150 F (see Figure 31). The influence of strain on the aging characteristics is summarized in Figure 32. As the strain is increased, the driving force for hydrogen diffusion from the lattice to the voids is increased. Also, as the strain is increased, the level of ductility observed at the minimum at the end of the second stage of aging is increased and displaced to longer aging times. This observed behavior can be accounted for by two factors - the depletion of the lattice hydrogen content with increasing strain, and the increasing importance of outgassing at long aging times. Extrapolation of the shapes of the aging curves to larger strains suggested that the embrittlement will essentially disappear at a sufficiently large strain. This was found to be the case for specimens strained 12 per cent at -321 F and aged at 150 F, as shown in Figure 33. The recovery curve is a horizontal line at a level of ductility equal to, or only slightly below, the ductility of uncharged specimens.

It was concluded that the strain-induced recovery is due entirely to the redistribution of hydrogen, the gross hydrogen content of the specimens remaining constant during the process. For the test conditions used for the above-described experiments, 12 per cent strain increased the occlusive capacity of the voids enough to completely drain the lattice of damaging hydrogen in establishing the new steady-state distribution. On the other hand, these investigators found that elastic straining did not affect the aging characteristics, for unstrained and elastically strained specimens exhibited identical aging curves. This is striking evidence of the localized redistribution of hydrogen resulting from plastic deformation.

The aging characteristics exhibited after room-temperature straining also were studied. Premature crack formation limited strain of the hydrogenated steel at room temperature to 0.2 per cent reduction in area. Qualitatively, room-temperature straining exerted the same effect as straining at -321 F, but the magnitude of the effect was

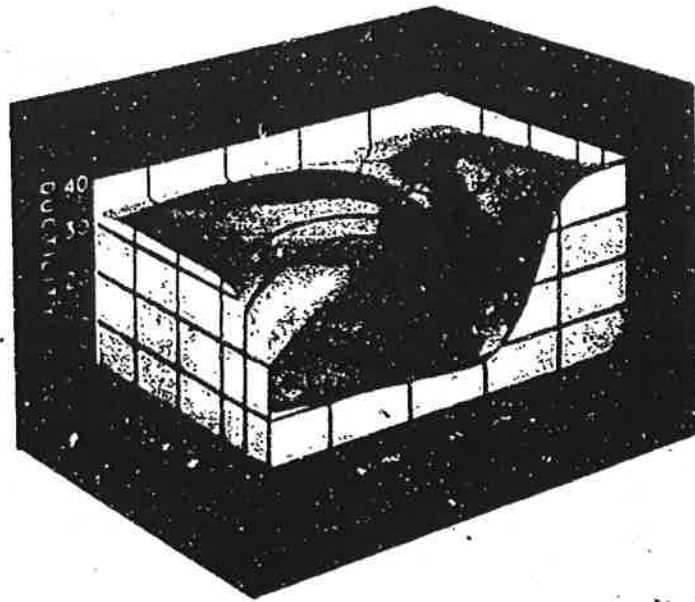


FIGURE 32. AGING CHARACTERISTICS OF SPECIMENS STRAINED DIFFERENT AMOUNTS IN LIQUID NITROGEN AFTER CHARGING⁽⁴⁴⁾

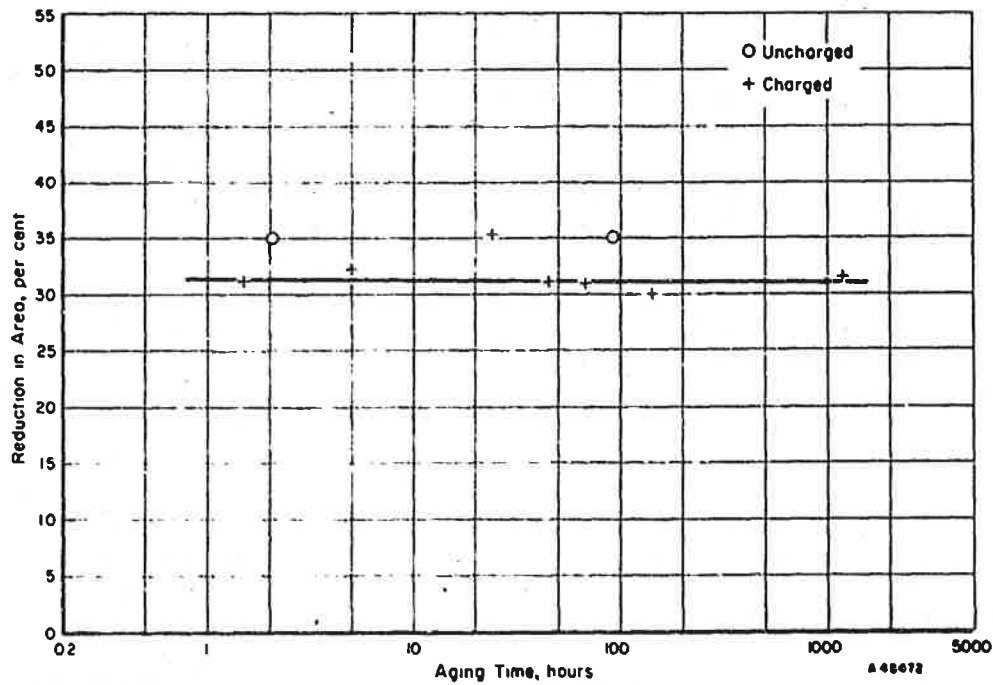


FIGURE 33. THE EFFECT OF AGING AT 150 F ON SPECIMENS STRAINED 12 PER CENT IN LIQUID NITROGEN⁽⁴⁴⁾

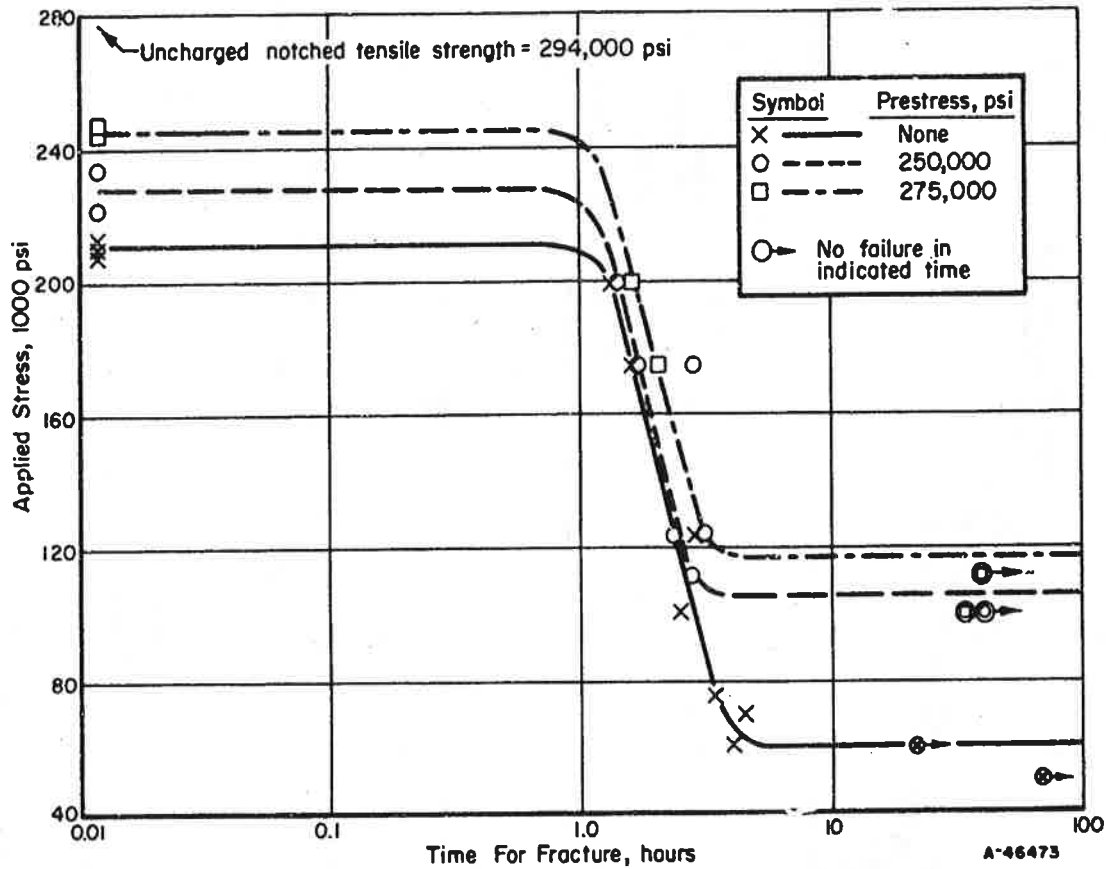


FIGURE 34. DELAYED-FAILURE BEHAVIOR FOR VARIOUS LEVELS OF PRESTRESSING FOR SHARP-NOTCH SPECIMENS AT THE 240,000-PSI STRENGTH LEVEL⁽⁴⁵⁾

Charged after prestressing.

Aged 5 minutes at room temperature.

Case Institute of Technology Charging Condition A:

Electrolyte: 4 per cent H_2SO_4 in water

Poison: None

Current density: 20 ma/in. ²

Charging time: 5 minutes

Aging time: Measured from end of charging to start of test.

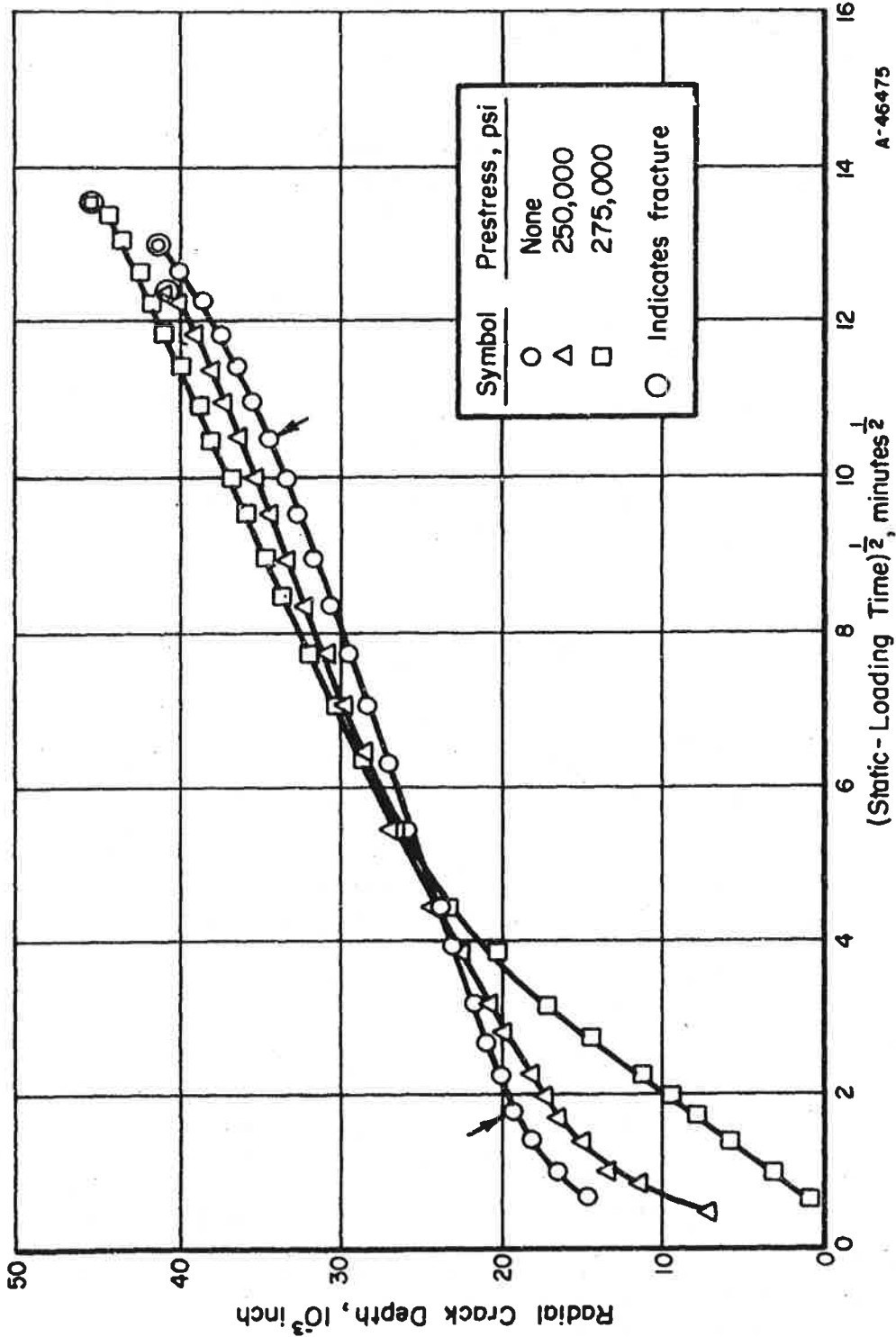


FIGURE 36. RADIAL CRACK DEPTH VERSUS THE SQUARE ROOT OF THE STATIC-LOADING TIME AT AN APPLIED STRESS OF 125,000 PSI FOR VARIOUS LEVELS OF PRESTRESSING OF SPECIMENS HEAT TREATED TO THE 240,000-PSI STRENGTH LEVEL(45)

Case Institute of Technology Charging Condition A, as given in Figure 34.

failures depend directly on the hydrogen content. If the hydrogen can be kept out or removed from the steel before the part is subjected to conditions which result in permanent damage, the problem is circumvented. However, this is not easy to do because of the numerous processing operations that are potential sources of hydrogen and because of the very small amount of hydrogen (as little as 1 ppm, or possibly less) that can induce failure. Another important point that has been demonstrated numerous times is that, although baking to "remove" hydrogen can result in full recovery of ductility as determined in a standard tensile test, frequently such a treatment is not sufficient to prevent delayed failure at a low stress under conditions of static loading.

Bucknall, Nicholls, and Toft⁽⁴⁷⁾ reported encountering delayed failures in several high-strength steels without the intentional introduction of hydrogen after heat treatment and with no obvious source of hydrogen, such as acid pickling or an electroplating operation, being used after heat treatment. They did not recognize that hydrogen was the culprit. Conical disk specimens similar to Bellville springs were compressed by tightening a bolt and then were observed periodically, usually for 100 days. The most important factor governing the tendency to crack after some time delay appeared to be the hardness of the plate. There was a hardness below which, under the conditions of stressing, no specimens cracked during the 100-day test period. For a given material, at some higher hardness all specimens cracked, and at some intermediate hardness, some specimens cracked and others did not, the proportion which cracked rising as the hardness increased. For all steels examined, the water-quenched condition was most susceptible to delayed cracking, the oil-quenched condition was less susceptible, and the tempered material was least susceptible. The following example shows the results for a Ni-Cr-Mo-V steel.

<u>Hardness, BHN</u>	<u>Number of Specimens Tested</u>	<u>Number Cracked Within 100 Days</u>	<u>Proportion Cracked Within 100 Days, per cent</u>
>521	1	1	100
491-520	5	4	80
461-490	13	8	60
431-460	11	0	0
401-430	2	0	0

The investigators concluded that every precaution should be taken to reduce internal stresses, and the plates should be used at the minimum hardness consistent with the required properties.

Barnett and Troiano⁽⁶⁾ showed that the susceptibility to delayed failures which Bucknall et al. observed was most prevalent when the material in processing had been subjected to an environment conducive to the absorption of hydrogen.

Bell and Sully⁽⁴⁸⁾ also obtained delayed failures in a high-strength steel without intentionally charging it with hydrogen after heat treatment. However, these investigators also introduced hydrogen electrolytically in other specimens of the same steel and obtained delayed failures at far lower stresses. They studied a plain-carbon steel (0.8 to 0.9 per cent carbon) at hardness levels of approximately 560 DPN and approximately 500 DPN. Static stresses were obtained in bending by using a Seeger-circlip specimen, one end of which was held stationary and the other end moved away from the fixed end by a screw arrangement with a vernier scale attached. As stress relieved for 24 hours at 160 C (320 F), the average breaking deflection was 1.110 inch. When

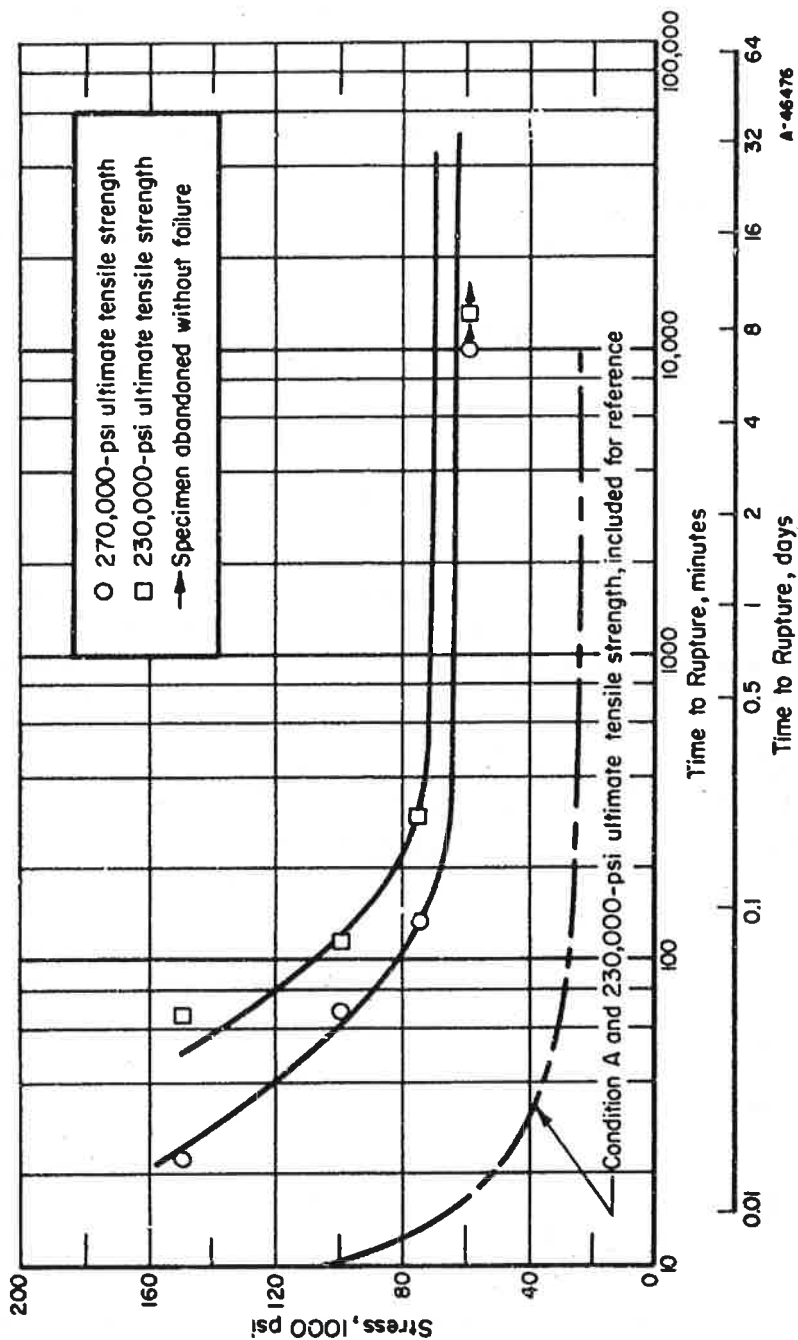


FIGURE 37. DELAYED-FAILURE BEHAVIOR OF AN SAE 4340 STEEL DURING CATHODIC CHARGING IN AN ACETIC ACID ELECTROLYTE AT 1 MA/IN.²(8)

Battelle Charging Condition B:

Electrolyte: 10 per cent acetic acid, 45 per cent ethylene glycol,
 and 45 per cent water by volume
 Current density: 1 ma/in.².

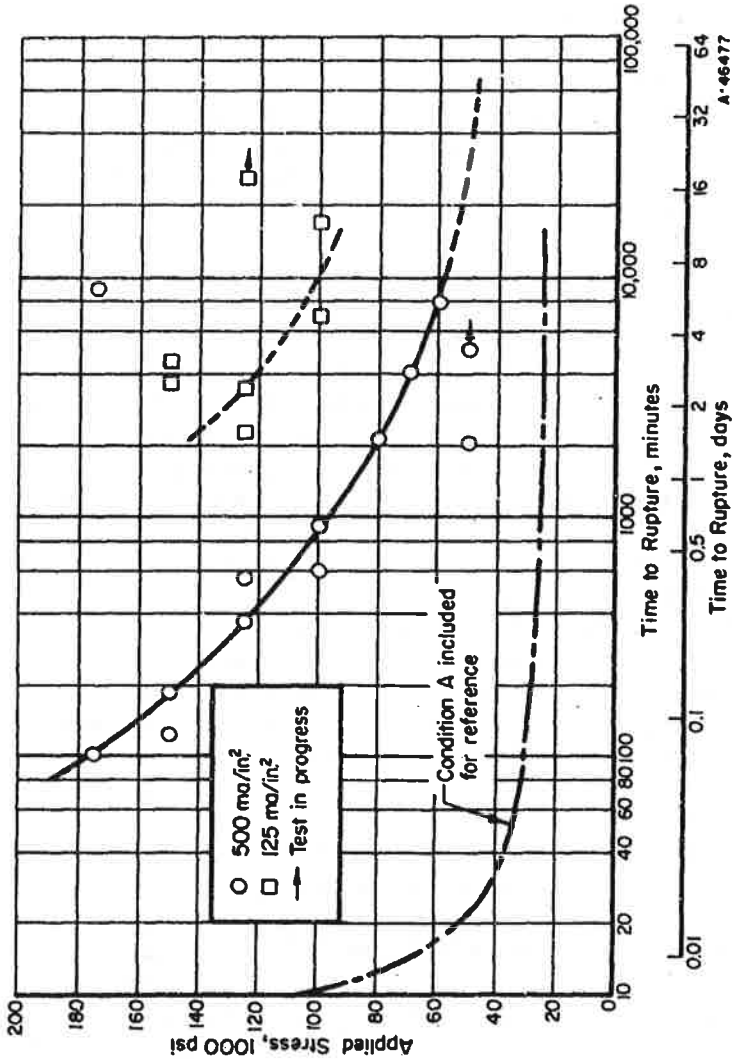


FIGURE 38. DELAYED-FAILURE BEHAVIOR OF AN SAE 4340 STEEL WITH AN ULTIMATE STRENGTH OF 230,000 PSI DURING CATHODIC CHARGING IN A 1/2 PER CENT SODIUM HYDROXIDE ELECTROLYTE(8)

Battelle Charging Condition C:

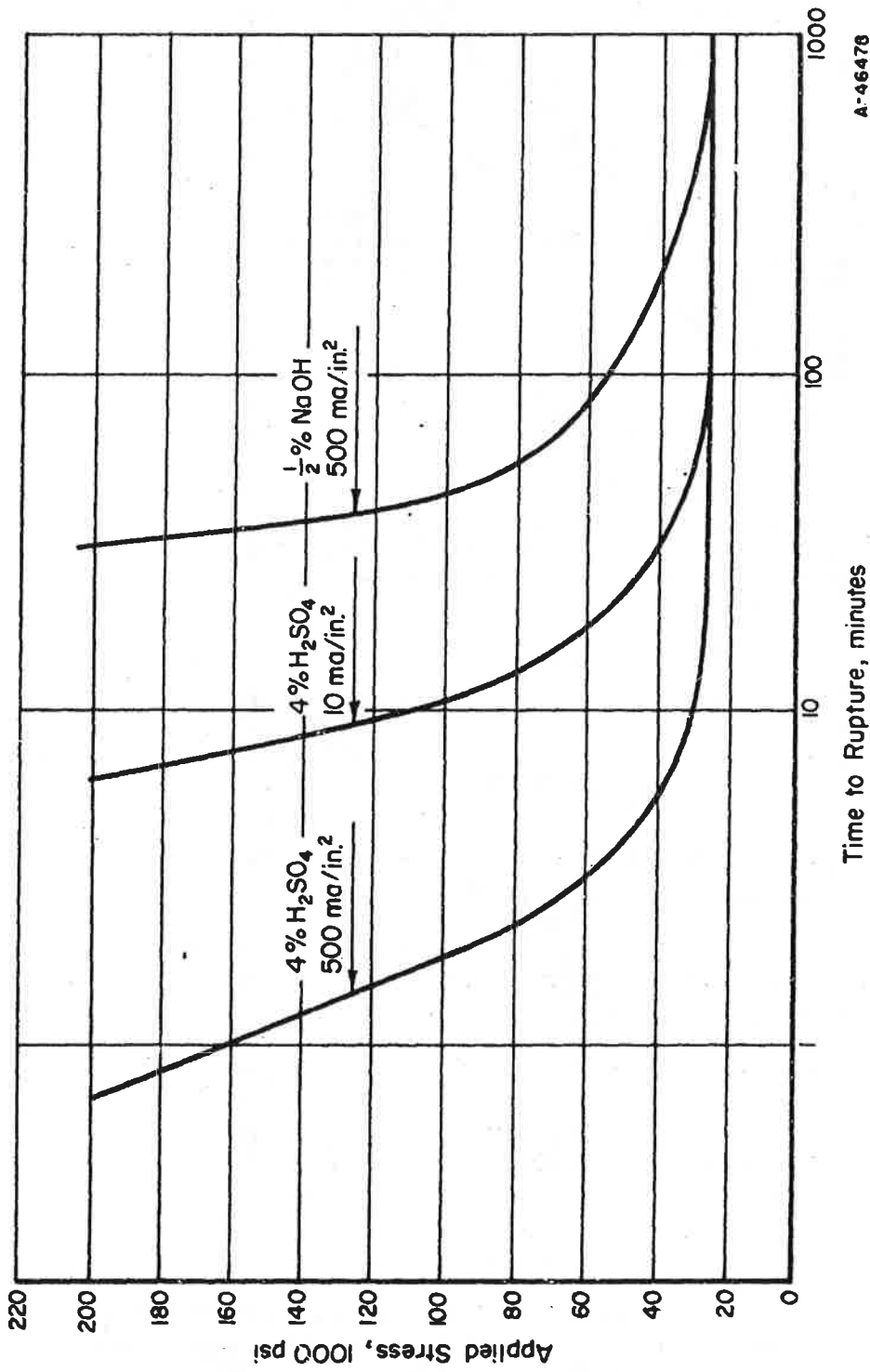
Electrolyte: 1/2 per cent sodium hydroxide in water

Current density: 125 ma/in. ².

Battelle Charging Condition D:

Electrolyte: 1/2 per cent sodium hydroxide in water

Current density: 500 ma/in. ².



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FIGURE 39. TIME FOR FAILURE AS A FUNCTION OF APPLIED STRESS FOR VARIOUS CHARGING CONDITIONS(9)

SAE 4340 steel, 230,000-psi ultimate tensile strength

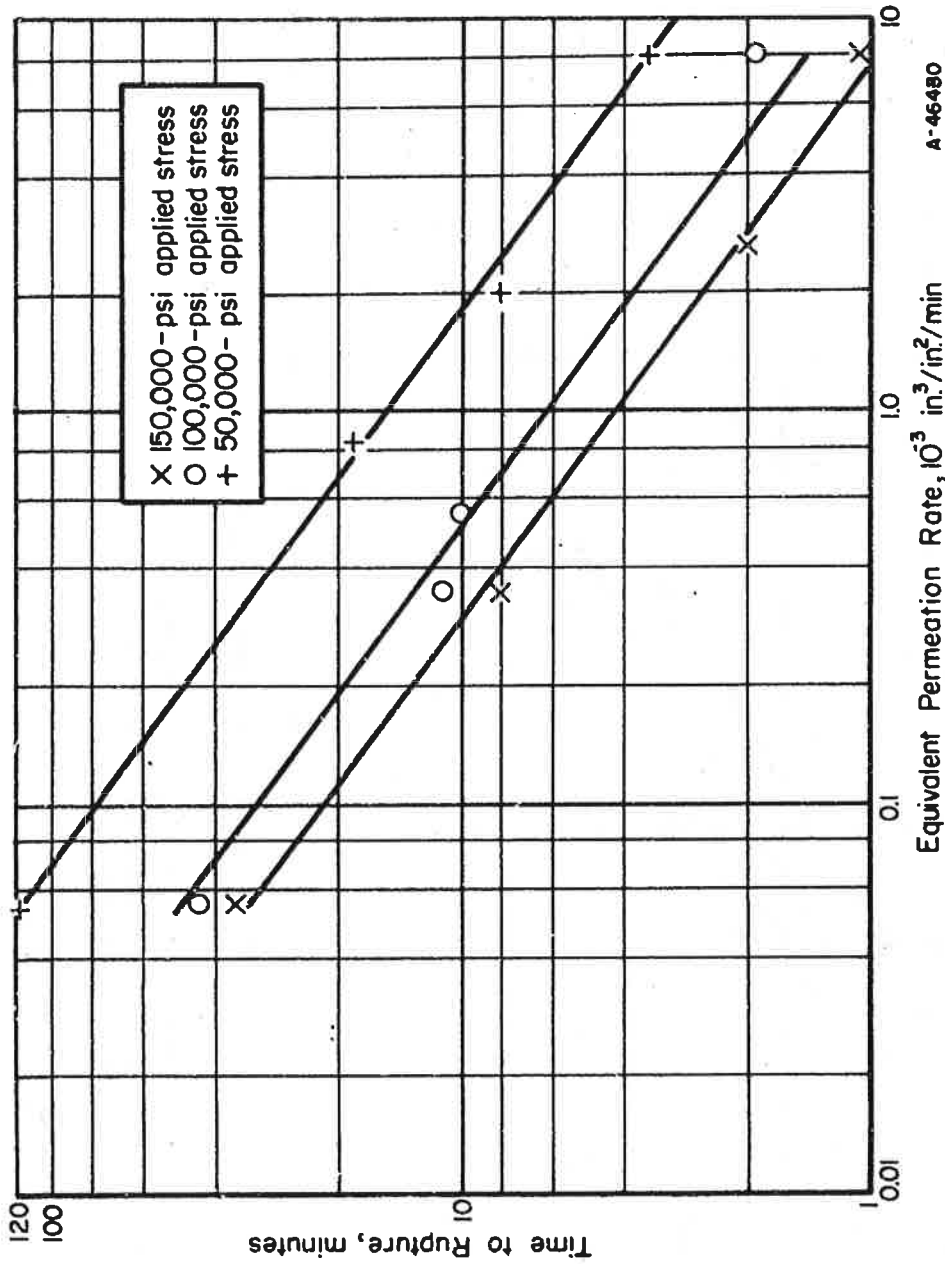


FIGURE 41. RUPTURE TIME FOR THE 230,000-PSI-STRENGTH STEEL AS A FUNCTION OF THE CATHODIC CHARGING CONDITION WHERE THE CHARGING CONDITION IS DEFINED AS THE EQUIVALENT PERMEATION RATE THROUGH A 0.010-INCH SPECIMEN(9)

.SAE 4340 steel.

which hydrogen is introduced into the steel. The curves shown in Figures 41 and 42 can be expressed by the equation

$$T_f = K \cdot P^n,$$

where

T_f = time for failure to occur

P = permeation rate

K, n = constants.

The slopes (the constant n) of the nearly parallel lines for the steel with 230,000-psi ultimate tensile strength were approximately -0.7 , while those for the curves for the 190,000-psi strength level were approximately -0.6 . Since n showed such little variation with changes in ultimate tensile strength, it was suggested that an average value of approximately $-2/3$ might more adequately describe the reaction. No physical significance was attached to the values obtained for these slopes.

It is evident from Figures 41 and 42 that variations in the rate at which hydrogen was introduced into the steel had a greater effect on the rupture time than did variations in the applied stress, except when the applied stress was near the minimum critical stress for failure. Variations in the absorption rate had about as great an influence on the rupture time as did variations in the ultimate tensile strength of the steel. Since it is possible to obtain even wider ranges of hydrogen-charging conditions than those investigated, it appears that much greater variations in rupture time can be obtained by varying the rate at which hydrogen is introduced into the steel than can be obtained by altering the strength level of the steel. From this, one might conclude that the rate at which hydrogen is charged into a steel specimen is the most significant factor in producing delayed, brittle failures. However, in practice, much less hydrogen is introduced into a part during pickling and cleaning operations than was introduced into the tensile specimens of this investigation. Therefore, it was concluded that the strength level of the steel probably is the most important factor after all in practical considerations of delayed, brittle failure.

The bend tests performed by Slaughter et al. (8) which were described previously in discussing the effects of applied stress, also were useful in determining whether delayed failures are dependent on the hydrogen content or on the total quantity of hydrogen which traverses a given region by diffusion. Specimens stressed in bending were charged only on the compression side, and the tension side was notched so that the thickness of the specimens at the base of the notch varied from 0.075 inch to 0.250 inch. These specimens were cathodically charged in 4 per cent sulfuric acid electrolyte with added poison at a current density of approximately 33 ma/in.². Under these conditions, a hydrogen gradient was established through the specimen, with the hydrogen content being highest at the cathodically charged compression surface and lowest at the tension surface where hydrogen was escaping to the atmosphere. As shown in Figure 26 (page 43), one specimen failed after a delay of 15 days. Since this specimen was only 0.075 inch thick at the minimum section, the steady-state concentration gradient of hydrogen should have been obtained in approximately 400 minutes as shown by permeability experiments for the conditions used. Therefore, the period for establishing the necessary hydrogen content within the specimen was a very small portion of the 15-day delay.

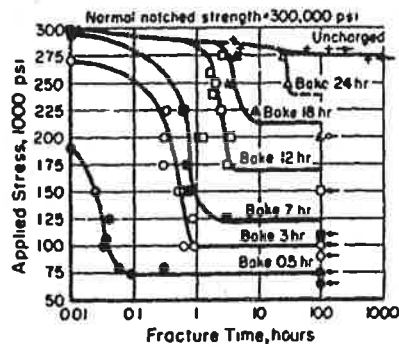


FIGURE 43. DELAYED-FAILURE BEHAVIOR FOR VARIOUS HYDROGEN CONCENTRATIONS CORRESPONDING TO DIFFERENT BAKING TIMES AT 300 F⁽⁴⁹⁾

Sharp-notch specimens, SAE 4340 steel, 230,000-psi strength level

Case Institute of Technology Charging Condition A:

Electrolyte: 4 per cent H₂SO₄ in water

Poison: None

Current density: 20 ma/in.²

Charging time: 5 minutes.

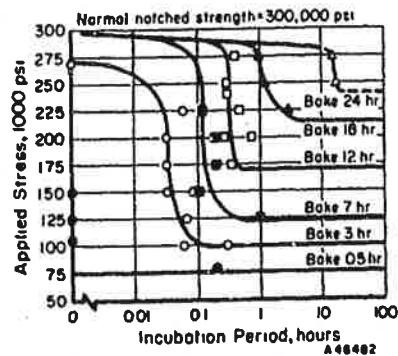


FIGURE 44. VARIATION OF INCUBATION PERIOD WITH APPLIED STRESS AND HYDROGEN CONCENTRATION CORRESPONDING TO DIFFERENT BAKING TIMES AT 300 F⁽⁴⁹⁾

Sharp-notch specimens, SAE 4340 steel, 230,000-psi strength level.

Case Institute of Technology Charging Condition A, as in Figure 43.

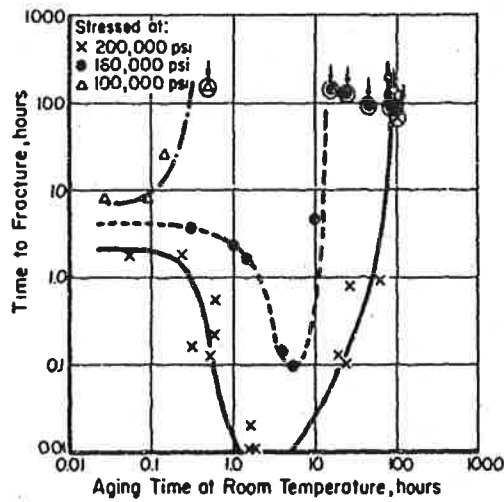


FIGURE 45. EFFECT OF AGING TIME AT ROOM TEMPERATURE ON TIME TO FRACTURE FOR SAE 4340 STEEL HEAT TREATED TO 230,000 PSI⁽⁵⁾

Sharp-notch specimens. Case Institute of Technology Charging Condition A, as in Figure 43.

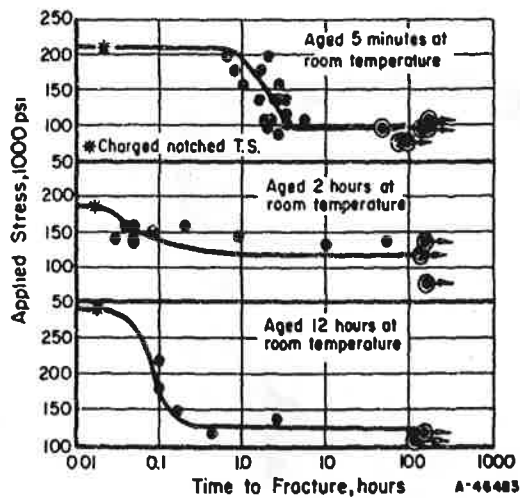


FIGURE 46. STATIC-LOADING TESTS ON SAE 4340 STEEL HEAT TREATED TO 270,000 PSI AND AGED AS INDICATED⁽⁵⁾

Sharp-notch specimens. Case Institute of Technology Charging Condition A, as in Figure 43.

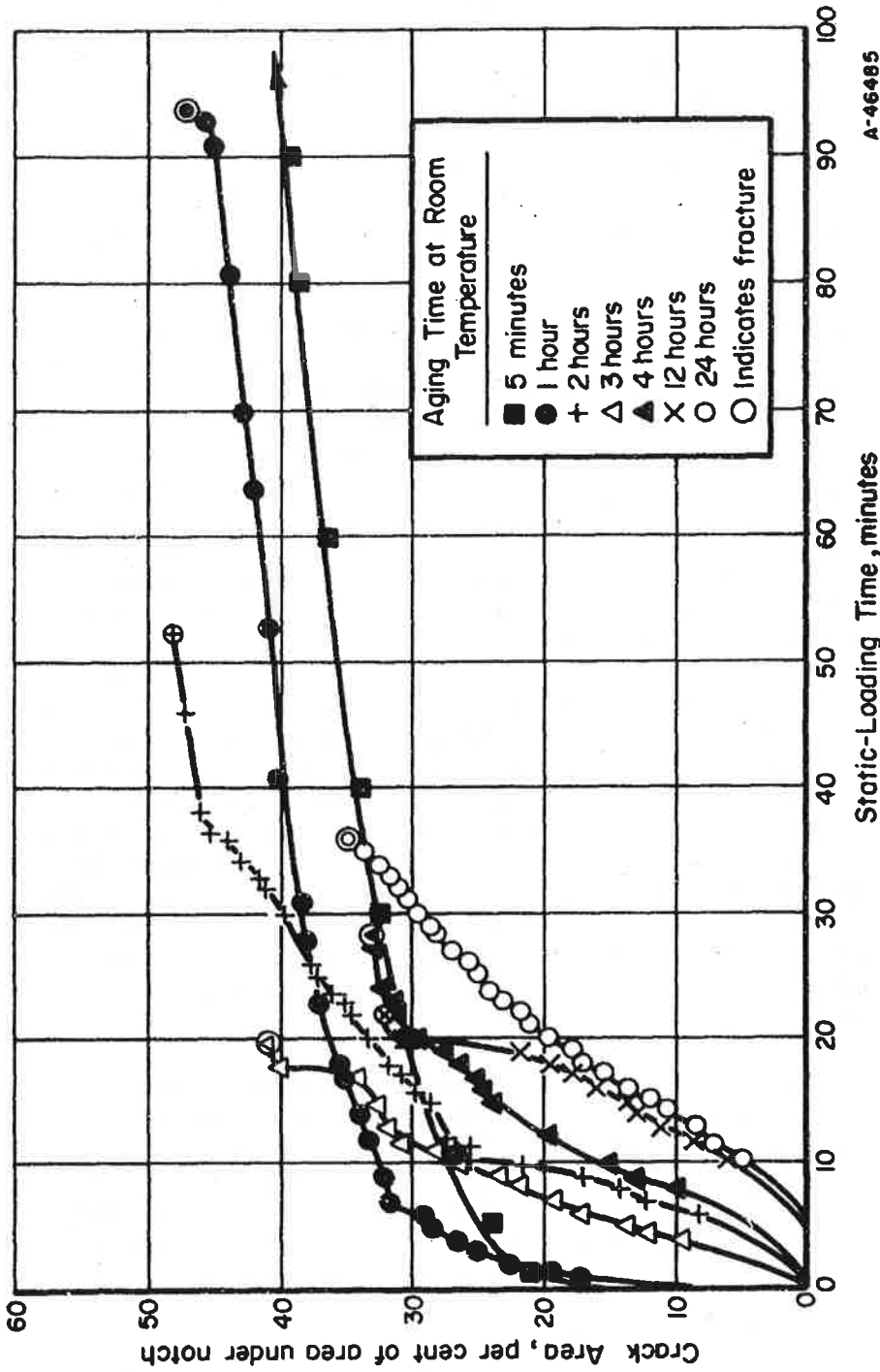


FIGURE 49. EFFECT OF PRIOR ROOM-TEMPERATURE AGING ON CRACK PROPAGATION IN SAE 4340 STEEL AT AN APPLIED STRESS OF 175,000 PSI(39)

Sharp-notch specimens. Case Institute of Technology Charging Condition A, as in Figure 43.

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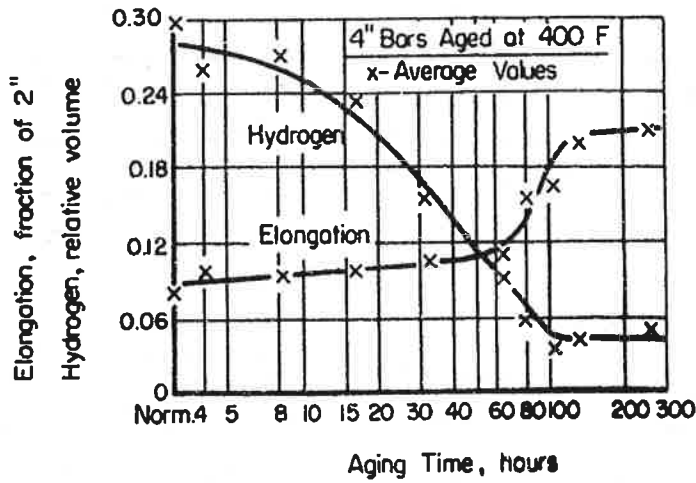


FIGURE 50. COMPARATIVE CHANGE OF HYDROGEN AND DUCTILITY DURING AGING(52)

Values for center of cast steel bars.

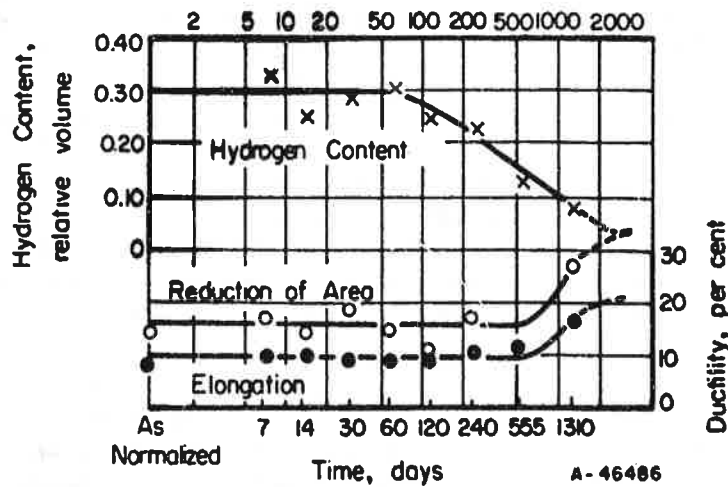


FIGURE 51. LOSS OF HYDROGEN FROM CENTER OF 4-INCH-SQUARE CAST-STEEL COUPONS AGED AT ROOM TEMPERATURE, AND EFFECT ON DUCTILITY(53)

its brittleness on that of the steel if the thickness of the base is not great enough compared with the thickness of the plate. Baking treatments were effective in recovering the original ductility.

Potak⁽⁵⁷⁾ presented experimental results concerning the embrittlement of a hardened high-carbon steel by a number of different electrolytic treatments. Figelman and Shreider⁽⁵⁸⁾ studied the effects of electroplating with chromium, copper, nickel, zinc, and cadmium on the ductility of heat-treated spring steel. The testing method consisted of measuring the bend angle necessary to produce failure of a flat specimen. They found that aging at 200 to 300 C (390 to 570 F) was almost always effective in recovery of ductility, but in the case of high stresses, a higher temperature was necessary for their removal.

From these few references and the results of some of the investigations described previously in this report, it is apparent that sufficient hydrogen is introduced into steel during a commercial-type electroplating process to cause substantial embrittlement and to cause delayed, brittle failure under many conditions.

Other work has shown that frequently more hydrogen is introduced in acid pickling to remove scale or in cathodic cleaning prior to electroplating than is introduced in electroplating itself⁽⁵⁹⁾. These sources of hydrogen will be discussed more fully in a separate report.

Sachs and co-workers⁽¹⁹⁾ performed hydrogen analyses on cadmium-plated sustained-load-type specimens of seven different high-strength steels. The analyses were obtained by cooling specimens in dry ice immediately after electroplating and keeping them at this reduced temperature until they were analyzed. The average hydrogen content for cylindrical stress-rupture specimens was approximately 2.5 ppm. Within the scatter of the data, steel composition had no effect on the amount of hydrogen contained in the specimen after cadmium electroplating. Comparison with earlier work where hydrogen was charged electrolytically without metal plating showed that hydrogen introduced into specimens during cadmium electroplating may be as high as that introduced through severe cathodic impregnation. The hydrogen content was shown to vary with section size, as would be expected.

Hobson and Sykes⁽⁴²⁾ showed that electrolytic charging and the introduction of hydrogen under pressure at 600 C (1112 F) gave the same embrittling effect, as measured by reduction in area.

R. D. Johnson et al.⁽⁶⁰⁾ showed that the delayed-failure behavior was almost identical for commercial cadmium-plated steel and the same steel cathodically charged with hydrogen under their Charging Condition A, for short-time aging (5 minutes) at room temperature. Figure 53 shows their results. At the 230,000-psi strength level, both methods of introducing hydrogen led to nearly identical delayed-failure curves (Figure 53b). The correlation at the 270,000-psi strength level is not as obvious, since sharp-notched specimens were used for cathodic charging, while specimens with a notch radius of only 0.010 inch were used for commercial cadmium plating. Allowing for the difference in notched tensile strength between the specimens with the two different notch radii, they concluded that the stress displacement of the delayed-failure curves in Figure 53a probably resulted from the difference in notch radii.

Schuetz and Robertson⁽²⁵⁾ obtained a similar loss in ductility either from exposure to H₂S solution or from cathodic charging. A number of other investigators have studied the hydrogen embrittlement and delayed, brittle fractures of steel resulting from exposure to H₂S⁽⁶¹⁻⁶⁷⁾.

Time-dependent delayed failures have been observed in rocket-motor cases when tested at constant pressure and exposed to aqueous environments^(68, 69). The first motor case failed unexpectedly on being pressure tested with water at intervals over a period of several months. In a series of experiments on small-size pressure vessels, both oil and water were used in pressure testing, and tests were performed under the following conditions:

- (1) No protection
- (2) Inside of vessel coated with primer, outside submerged in water bath
- (3) Inside and outside coated with primer.

When the metal was not allowed to come in contact with an electrolytic solution, failure occurred at high tangential stresses. Also, it was possible to transfer the origin of the fracture from the inside to the outside surface by protecting the inside and exposing the outside to the water. Thus, it was proved that the water used in hydrostatic testing was the cause of failure and that these failures were induced by hydrogen. Hydrogen embrittlement lowered the burst strength by 130,000 psi or more. These workers suggested that the role of water was twofold: (1) It provided the pit which, in turn, provided the essential triaxiality of stress, and (2) It was a medium for localized galvanic action which released the essential atomic hydrogen.

Spaeth concluded that hydrotesting with oil is an effective preventive measure against embrittlement, provided that the pressure-vessel steel is not loaded with hydrogen prior to hydrostatic testing.

Norton⁽⁷⁰⁾, using heavy water (D₂O), showed that the hydrogen in water participates in the initial corrosion of steel, rather than the hydrogen present in the steel.

Steigerwald⁽⁷¹⁾ carried out an investigation to systematically evaluate the influence of liquid environments (primarily aqueous) on the delayed-failure characteristics of high-strength steel in the presence of very sharp notches (fatigue cracks). This work was performed to help determine (1) whether or not slow crack growth was stimulated by the staining media sometimes used with precracked sheet tension tests for the measurement of the fracture-toughness parameter and the notched tensile strength of ultra-high-strength steels, and (2) whether any such stimulation affected the fracture toughness and strength values obtained.

A low-alloy martensitic steel (300M) and an H-11 type hot-work die steel were used in the investigation. The compositions, and the tensile properties for the various conditions of heat treatment used, are listed in Tables 11 and 12, respectively. Details of the precracked center-notch tensile specimen are given in Figure 54. The results of static-load tests on 300M steel with distilled water and recording ink as the environment are shown in Figures 55 and 56. Results for the H-11 steel in distilled water are shown in Figure 57. Both liquid media produced a considerable range of time for failure, depending on the level of applied stress. Failures occurred at a fraction of the notched

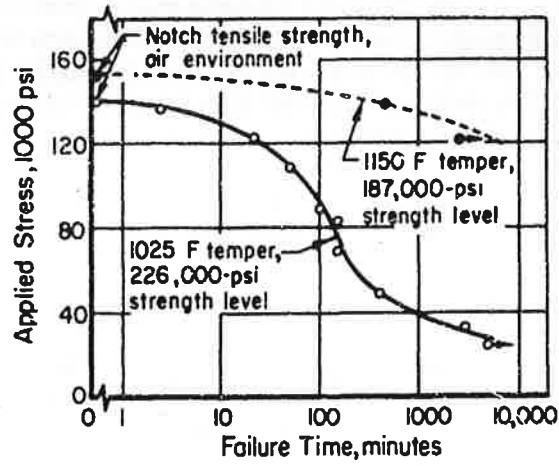


FIGURE 56. DELAYED FAILURE OF 300M STEEL CENTER-PRECRACKED SPECIMENS WHEN SUBJECTED TO A DISTILLED-WATER ENVIRONMENT⁽⁷¹⁾

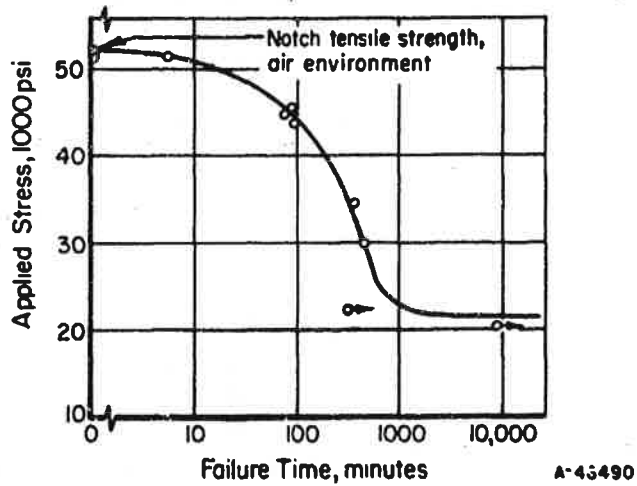


FIGURE 57. DELAYED FAILURE OF H-11 TOOL STEEL CENTER-PRECRACKED SPECIMENS AT THE 295,000-PSI-STRENGTH LEVEL WHEN SUBJECTED TO A DISTILLED-WATER ENVIRONMENT⁽⁷¹⁾

The data obtained were not sufficient to allow the particular mechanism or combination of factors to be defined conclusively. He considered that, in view of the fact that cracks were present and the organic environments caused delayed cracking, the mechanism involving a decrease in surface energy (Petch and Stables, 1952, Reference 72) was attractive. The apparent absence of an incubation time which he observed also is a necessary, but not sufficient, condition for a surface-adsorption mechanism. Therefore, a test was conducted on a 300M specimen that was not precracked but merely had a center jeweler's sawcut with a terminal radius of approximately 0.005 inch. The specimen was loaded to 90 per cent of the normal notched tensile strength and subjected to a distilled-water environment. Failure occurred in 15.2 hours. He found it difficult to visualize how surface adsorption on the face of the sawcut could lower the failure stress. Since the sawcut itself did not extend and a crack had to be initiated, most probably below the surface where the triaxiality favors fracture, another mechanism besides surface adsorption must be rate controlling. He concluded that, although hydrogen embrittlement and stress corrosion have both been observed in these high-strength steels, the manner in which sufficient hydrogen is produced or stress corrosion takes place in the various environments must be determined before these factors can be used to explain the observed delayed-failure process.

Davis⁽⁷³⁾ has studied stress corrosion and hydrogen embrittlement in two low-alloy high-strength steels, 4330M and SAE 4340. With electron-microscope fractography techniques, he claimed to be able to detect slight differences between hydrogen-embrittlement and stress-corrosion fractures; gross differences can be detected among ductile, fatigue, and intergranular brittle fractures. He reported that hydrogen-embrittlement and stress-corrosion fractures both appear to be intergranular with respect to the prior austenite grain boundaries. Metallographic microstructural differences between hydrogen-embrittlement and stress-corrosion cracking are not clearcut. However, fractographic studies with the electron microscope indicate that the two processes may be fundamentally related.

Swets and Frank⁽⁷⁴⁾ have reported on the pickup of hydrogen from a hydrocarbon lubricant by steel ball bearings. Swets, Frank, and Fry⁽⁷⁵⁾ found that grinding or abrading steel caused hydrogen pickup, apparently from water vapor in the air or from the cutting fluid when the latter was used.

In addition to the effect of concurrently plating hydrogen with the metal plate, the plate has another effect. The presence of a more-or-less impermeable metal coating, such as cadmium, makes the evolution of hydrogen from the interior of the base metal more difficult; this may serve to aggravate the effects of embrittlement and delayed failure of electroplated steel. Although appropriate baking treatments may restore most or all of the ductility to the plated steel, often such a treatment does not overcome the propensity toward delayed, brittle failure.

As was discussed previously, R. D. Johnson et al.⁽⁶⁰⁾ showed that the delayed-failure behavior was almost identical for commercial cadmium-plated steel and the same steel cathodically charged with hydrogen, for the conditions used. However, the room-temperature aging characteristics of cadmium-plated and hydrogen-charged specimens were markedly different, as is shown in Figure 58. Ductility was recovered more slowly in the case of the cadmium-plated specimens. Figure 52 (page 76) shows that chromium plate serves as a barrier to hinder evolution of hydrogen on aging, and, hence, to hinder recovery of ductility. Figure 59⁽¹⁰⁾ for recovery by baking at 375 F shows

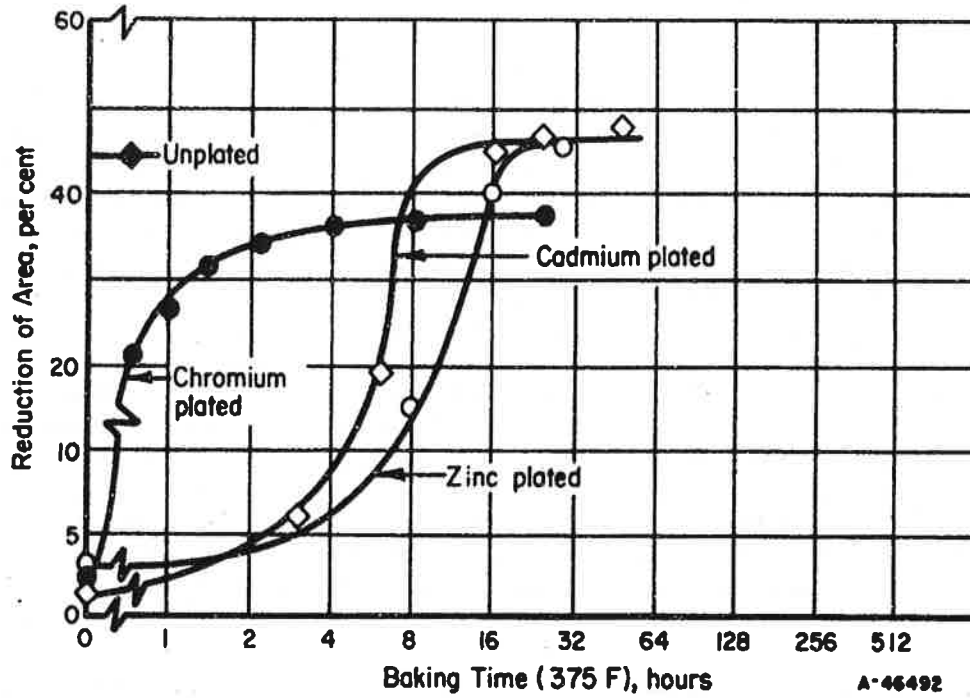


FIGURE 59. EFFECT OF BAKING TIME ON HYDROGEN EMBRITTLEMENT OF CHROMIUM-, CADMIUM-, AND ZINC-PLATED SPECIMENS(10)

Data by North American Aviation.

SAE 4340 steel, hardness = Rockwell C 45.

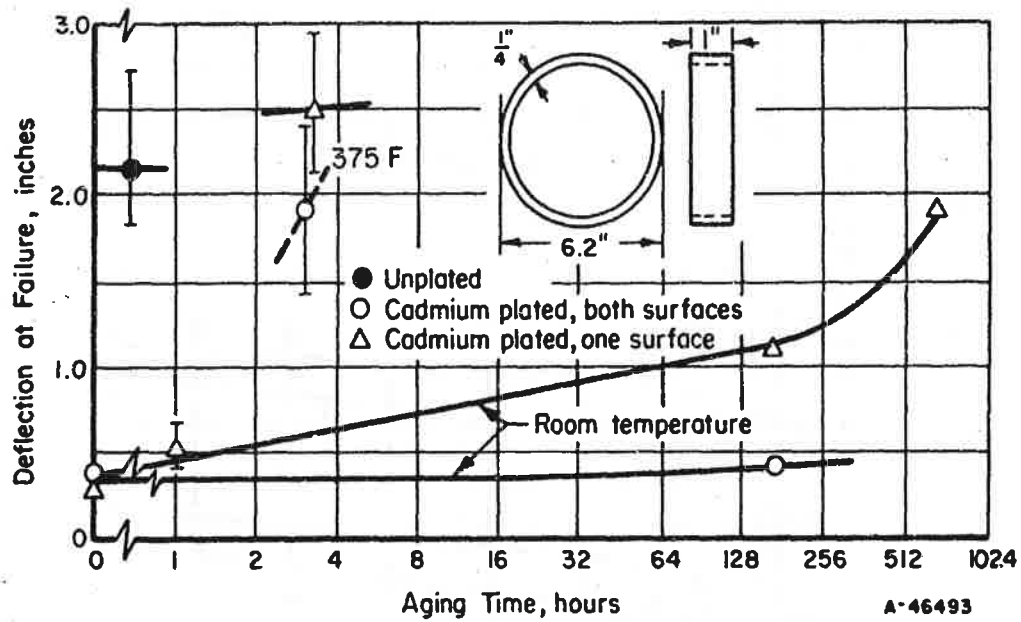


FIGURE 60. EFFECT OF ROOM-TEMPERATURE AGING AND BAKING AT 375 F ON HYDROGEN EMBRITTLEMENT OF CADMIUM-PLATED (0.001 INCH) STEEL TUBE(10)

Data by Menasco.

SAE 4340 steel; hardness = Rockwell C 50.

Before strength levels were boosted to the point where delayed, brittle failures were encountered in service, the most common relief practice for hydrogen embrittlement resulting from cadmium plating consisted of baking at 375 to 400 F for 3 or 4 hours. When hydrogen-induced delayed, brittle failures were encountered, baking times often were increased to 23 hours, but this practice was only partially effective. The effects of room-temperature aging and of baking on the susceptibility to delayed, brittle failures have already been discussed because of their use to produce different hydrogen contents for laboratory investigations of the phenomenon. Various investigators showed that, although suitable baking treatments resulted in recovery of lost ductility, frequently such treatments do not eliminate susceptibility to delayed failures, especially for materials of the higher strength levels; for example, see Figure 43 (page 69). Delayed failures have occurred after baking for times at least as long as 100 hours. It was shown that data obtained in a short-time tensile test are not suitable criteria of the susceptibility to delayed, brittle failure.

The recovery of parts cadmium plated on only one surface is considerably faster than that of parts plated on both sides. Figure 60 illustrates the difference for hollow parts plated in the one case only on the outer surface and in the other case on both surfaces. Occasionally, a specific lot of material is found which is especially resistant to the relief of hydrogen embrittlement. Often this is due to variations in the cadmium plate. A dense plate offers more resistance to the effusion of hydrogen than does a more porous plate. One factor influencing the type of plate produced is the use of a brightener in a cadmium-plating solution. One investigation showed that very small amounts of such an additive greatly reduced the recovery from hydrogen embrittlement of SAE 4340 steel heat treated to a hardness of Rockwell C 48. Also, some plating baths are more efficient than others and plate out less hydrogen at the metal surface. Such factors will be discussed more fully in a separate report being prepared on the movement of hydrogen in steel.

NEED FOR HYDROGEN MOVEMENT

A discussion of the chief requirements for delayed, brittle failures induced by hydrogen has been presented in preceding sections of this report. It has been shown that a critical combination of strength level, applied stress, and hydrogen content must be present in a region where failure can be initiated, usually in a region of triaxial stress state. Frequently, the necessary amount of hydrogen is not present at such a site, so movement of hydrogen must take place if failure is to be initiated. Also, as the failure propagates, the region of triaxial stress moves, so in most instances, hydrogen must move if propagation is to continue.

If hydrogen is to be free to move during the course of the failure, then conditions must be such as to favor diffusion of hydrogen. This, then, brings in considerations of temperature and time.

Hydrogen Movement Demonstrated

In the work of Frohberg et al. (5), laboratory delayed failures were induced in sharp-notch specimens of high-strength SAE 4340 steel which had been electrolytically precharged with hydrogen and then subjected to a sustained load. Although the amount

Frohberg et al. (5) showed that the diffusion of hydrogen plays a very important role in the delayed-brittle-failure phenomenon. During room-temperature aging prior to loading, outgassing, which decreases the total amount of hydrogen present, competes with the inward diffusion of hydrogen to establish the hydrogen distribution at the time of loading. This is shown in Figure 62. The hydrogen distribution is a factor in determining the delayed-failure characteristics. In the case of precharged notched specimens, the lower critical stress increases continuously with prior aging, because the available hydrogen concentration at the base of the notch is decreasing continually⁽⁵⁾. It was suggested that a critical combination of hydrogen and stress determines this limiting stress. However, as was shown previously, the notched tensile strength of charged specimens and the time to failure both pass through a minimum as a function of prior aging time after the same initial charging condition. Because of the relative insensitivity of the rupture time to strength level, it was suggested that the fracture time is related to the macroscopic diffusion of hydrogen inward from the initial surface concentration of electrolytically introduced hydrogen.

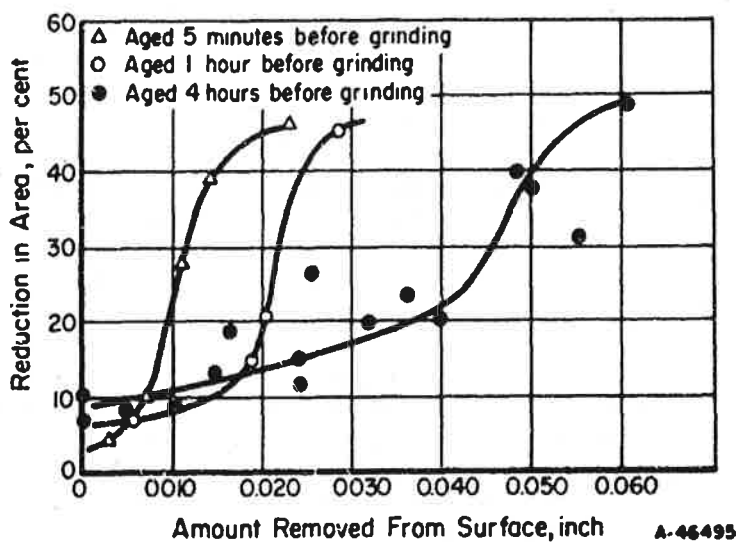


FIGURE 62. EFFECT OF REMOVING SURFACE LAYERS OF METAL FROM CHARGED UNNOTCHED TENSILE SPECIMENS AT THE 270,000-PSI STRENGTH LEVEL⁽⁵⁾

Case Institute of Technology Charging Condition A:

Electrolyte: 4 per cent H_2SO_4 in water
 Poison: None
 Current density: 20 ma/in.²
 Charging time: 5 minutes.

Barnett and Troiano⁽³⁹⁾ studied crack initiation and subsequent slow crack propagation of precharged notched specimens. For specimens aged 5 minutes at room temperature before loading, several important characteristics were observed that are related to the role of hydrogen in delayed failures. The specimens cracked (but did not

hydrogen-enriched region until it joins the previous crack. Further crack growth must wait for diffusion of hydrogen, induced by the stress gradient, to the new region of maximum triaxial stress.

Other work performed at Case Institute verified the concept that crack growth in hydrogenated steel is discontinuous in fashion. This has been discussed in the section dealing with the effects of applied stress and plastic strain.

These various results have served to show that the degree of embrittlement encountered and the rate of crack propagation attained in delayed, brittle failure are controlled by the diffusion of hydrogen.

The localized redistribution of hydrogen resulting from plastic deformation has been discussed previously in the consideration of the effects of applied stress and plastic strain. Also, the stress-induced diffusion of hydrogen has been discussed. Interpretation of the data obtained from studies of these two aspects of the movement of hydrogen is consistent with the hypothesis that hydrogen exerts a maximum embrittling effect in the region of most severe stress state. Hydrogen occluded in internal voids is purported to be nondamaging, and embrittlement apparently results from hydrogen in solution.

TABLE 14. FRACTURE STRESS AT VARIOUS APPLIED STRESSES AND HYDROGEN CONCENTRATIONS OBTAINED IN A STUDY OF THE IMPORTANCE OF HYDROGEN DIFFUSION IN DELAYED FAILURE(a)(49)

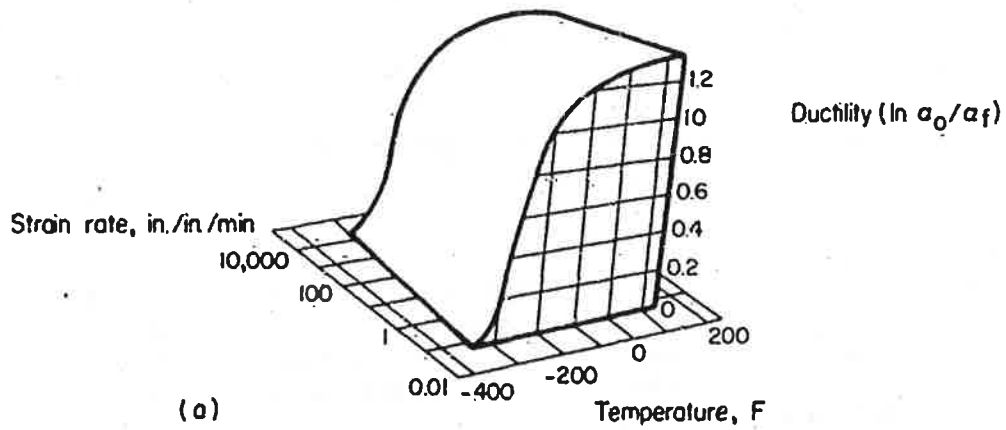
Baking Time(b), hours	Applied Stress, psi	Fracture Stress, psi
3	200,000	308,000
3	225,000	319,000
7	200,000	334,000
7	225,000	327,000
12	200,000	335,000
12	200,000	342,000
12	225,000	346,000
18	225,000	329,000

(a) Ultimate tensile strength, uncharged specimen = 230,000 psi.

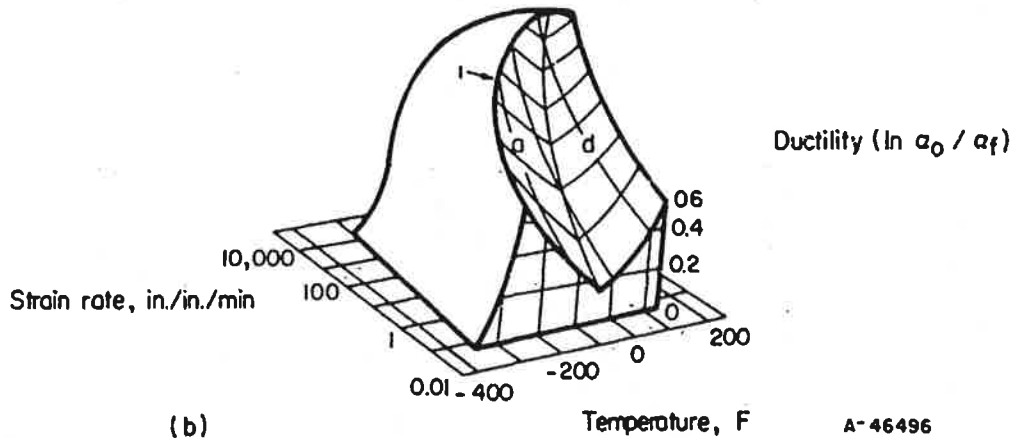
(b) The baking time was varied so as to provide different hydrogen concentrations.

Temperature Dependence

One of the unusual characteristics of hydrogen embrittlement is that the embrittlement disappears at low and high test temperatures and is, accordingly, most severe in an intermediate temperature range in the general vicinity of room temperature^(77,78).



(a)



(b)

A-46496

FIGURE 63. THE DUCTILITY OF AN SAE 1020 STEEL AS A FUNCTION OF STRAIN RATE AND TEMPERATURE (78)

(a) As annealed.

(b) As charged cathodically for 1 hr in 4 per cent sulfuric acid.

Curve i, in Figure 63b, bounds the range of strain rates and temperatures where embrittlement is found.

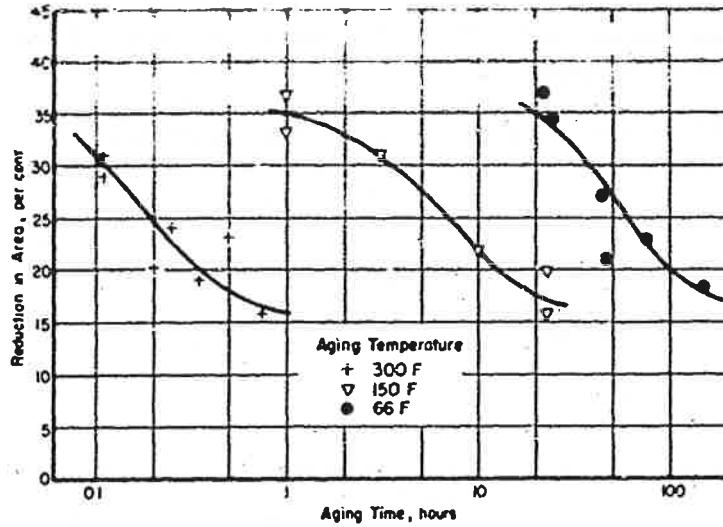


FIGURE 66. THE EFFECT OF AGING TIME AND TEMPERATURE ON THE RESULTING DUCTILITY IN THE SECOND STAGE OF AGING OF UNNOTCHED TENSILE SPECIMENS PREVIOUSLY CHARGED WITH HYDROGEN AND STRAINED 1.5 PER CENT IN LIQUID NITROGEN(44)

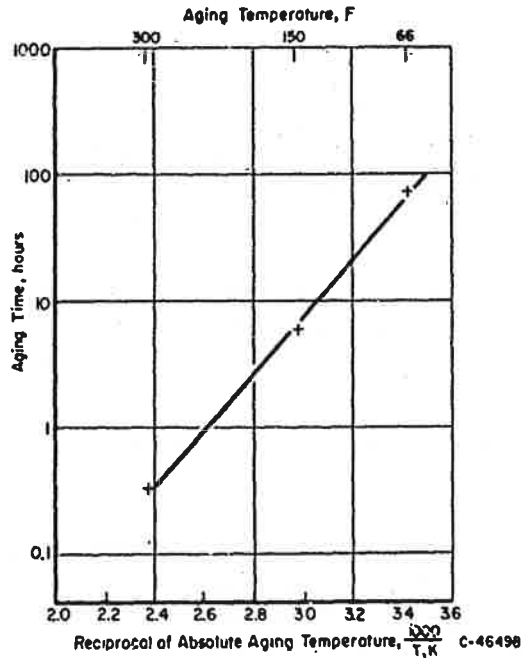


FIGURE 67. ARRHENIUS PLOT IN WHICH THE AGING TIME REQUIRED TO ACHIEVE HALF THE REDUCTION IN DUCTILITY ASSOCIATED WITH STAGE TWO OF AGING IS PLOTTED AGAINST THE RECIPROCAL OF THE ABSOLUTE AGING TEMPERATURE(44)
Activation energy 9600 cal/g.

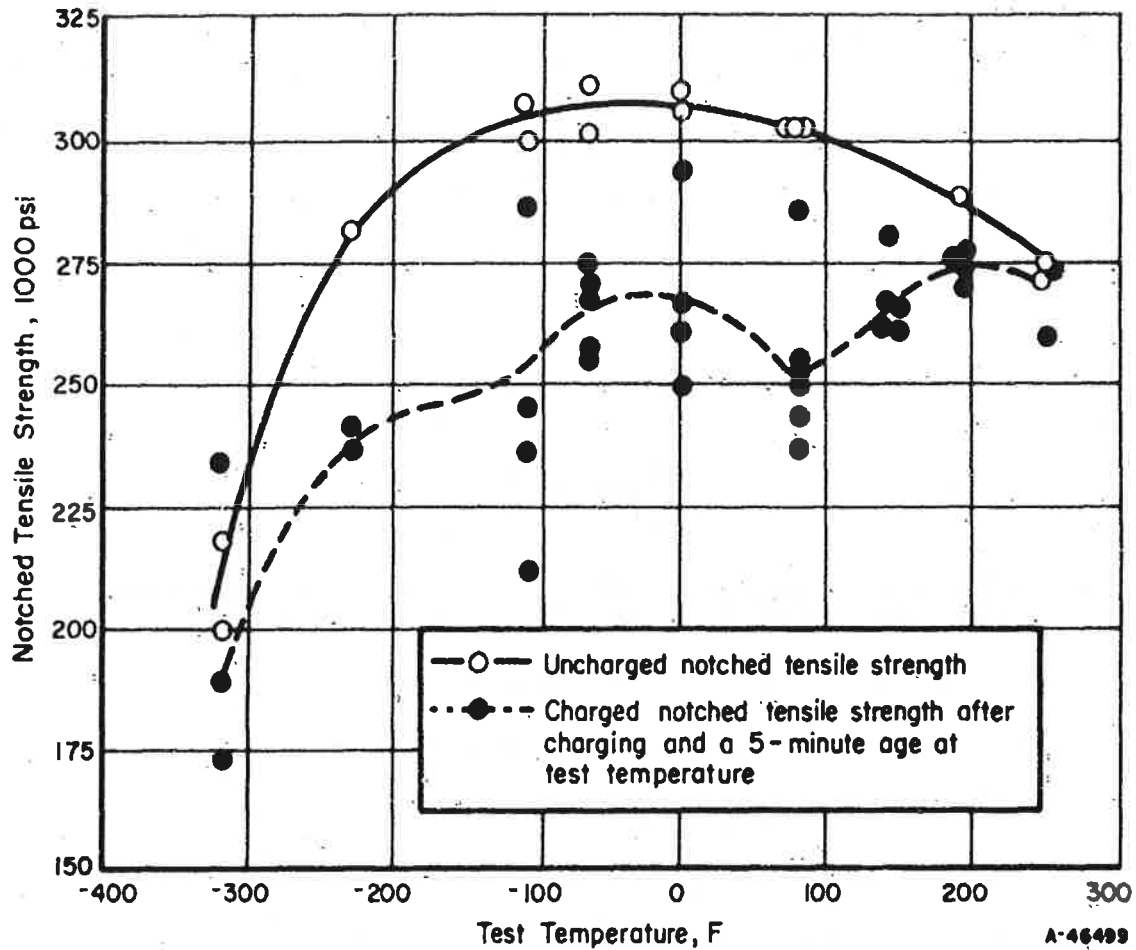


FIGURE 68. EFFECT OF TESTING TEMPERATURE ON THE NOTCHED TENSILE STRENGTH OF SAE 4340 STEEL IN THE CHARGED AND UNCHARGED CONDITIONS⁽⁶⁰⁾

230,000-psi strength level, sharp-notch specimens

Case Institute of Technology Charging Condition A:

Electrolyte: 4 per cent H_2SO_4 in water

Poison: None

Current density: 20 ma/in.²

Charging time: 5 minutes.

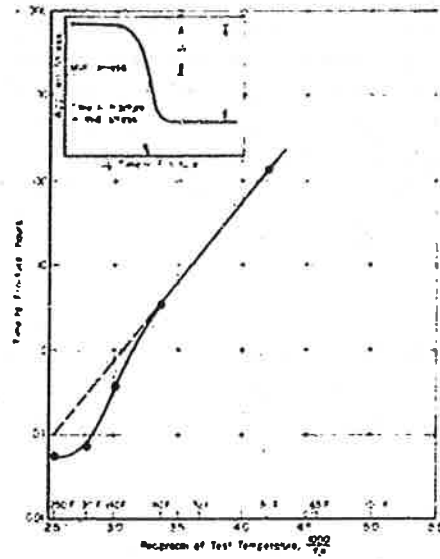


FIGURE 71. TIME FOR FRACTURE AS A FUNCTION OF RECIPROCAL OF ABSOLUTE TEST TEMPERATURE FOR SAE 4340 STEEL SPECIMENS AT 230,000-PSI STRENGTH LEVEL⁽⁶⁰⁾

Sharp-notch specimens aged 5 minutes at test temperature. Fracture time taken midway between upper and lower critical stresses as indicated.

Case Institute of Technology Charging Condition A, as in Figure 68.

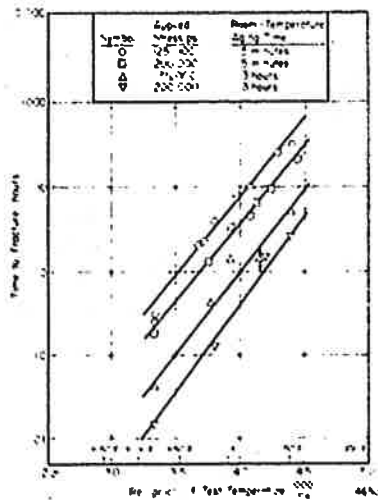


FIGURE 72. FRACTURE TIME VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE FOR CHARGED, SHARP-NOTCH SPECIMENS AT THE 230,000-PSI STRENGTH LEVEL, AGED AND STRESSED AS INDICATED⁽⁴⁵⁾

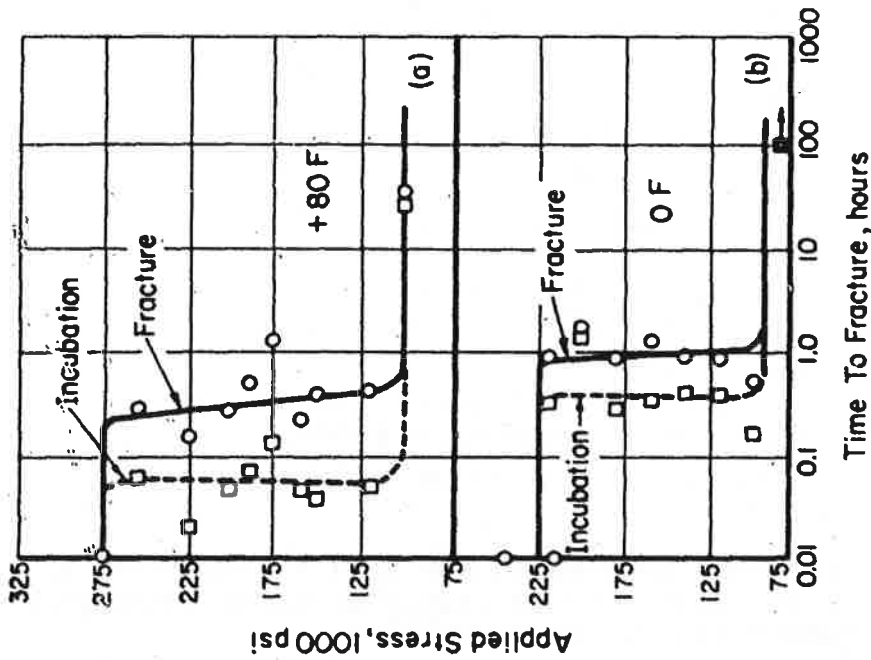


FIGURE 73. DELAYED-FAILURE BEHAVIOR OF HYDROGENATED HIGH-STRENGTH STEEL SPECIMENS TESTED AT 80 AND 0 F(80)

SAE 4340 steel heat treated to a tensile strength of 230,000 psi.

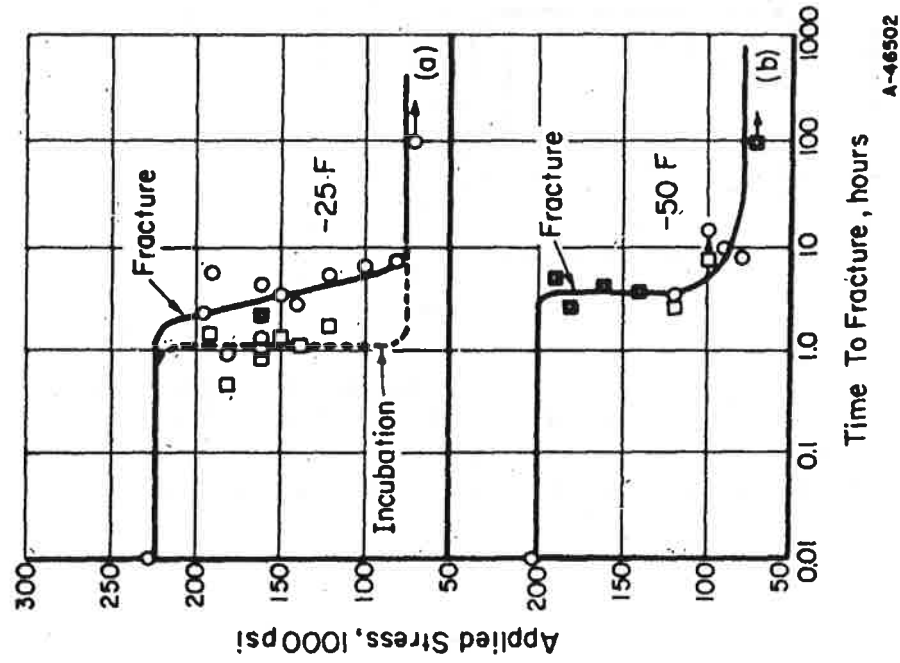


FIGURE 74. DELAYED-FAILURE BEHAVIOR OF HYDROGENATED HIGH-STRENGTH STEEL SPECIMENS TESTED AT -25 AND -50 F(80)

SAE 4340 steel heat treated to a tensile strength of 230,000 psi.

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temperatures at which hydrogen embrittlement is observed. For this reason, hydrogen embrittlement sometimes is referred to as low-strain-rate embrittlement. This has been discussed in a previous report (DMIC Memorandum 180), is shown in Figure 77, and has been summarized for SAE 1020 steel in Figure 63 (page 95). Hydrogen

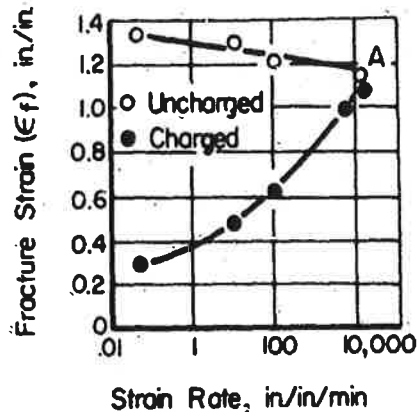


FIGURE 77. FRACTURE STRAIN AS A FUNCTION OF STRAIN RATE IN A CHARGED AND UNCHARGED, SPHEROIDIZED SAE 1020 STEEL AT ROOM TEMPERATURE⁽⁷⁷⁾

embrittlement of high-strength steel is nil in an impact test. It may or may not be detected in a standard tensile test of unnotched specimens, depending on the hydrogen content and distribution; however, it is more apparent in a notched tensile specimen with the triaxial stress state introduced by the notch. The most sensitive test for hydrogen embrittlement is the static-loading test of a notched specimen. According to the generally accepted mechanisms for hydrogen embrittlement and delayed, brittle fracture, the strain-rate dependence of hydrogen embrittlement reflects differences in the time available for hydrogen to diffuse into the highly stressed regions. In a test at high strain rates, such as an impact test, the time is not sufficient to permit a damaging amount of hydrogen to diffuse into the region of maximum triaxiality, and embrittlement does not develop. However, as the strain rate is decreased, more hydrogen can diffuse into the highly stressed region, and embrittlement tends to occur. The ultimate in this direction is achieved in the static-loading test where the strain rate is zero. Hydrogen diffuses very rapidly in ferritic or martensitic steels at room temperature, in fact, faster than most intermetallic diffusion at temperatures approaching the melting point of the solvent metal. Therefore, although the phenomenon is diffusion controlled, under many conditions severe embrittlement can be detected in an ordinary tensile test where the crosshead speed may be about 0.05 inch per minute and the test time may be in the neighborhood of 2 minutes. Thus, the accepted mechanism for hydrogen embrittlement is in agreement with the observed effects of temperature and strain rate.

The most sensitive test for revealing hydrogen embrittlement and the only satisfactory way to study delayed, brittle fracture is the static-loading test. Use of this test, of course, precludes a study of variations in strain rate. However, a few examples of the results of variations in strain rate on embrittled high-strength steels will be

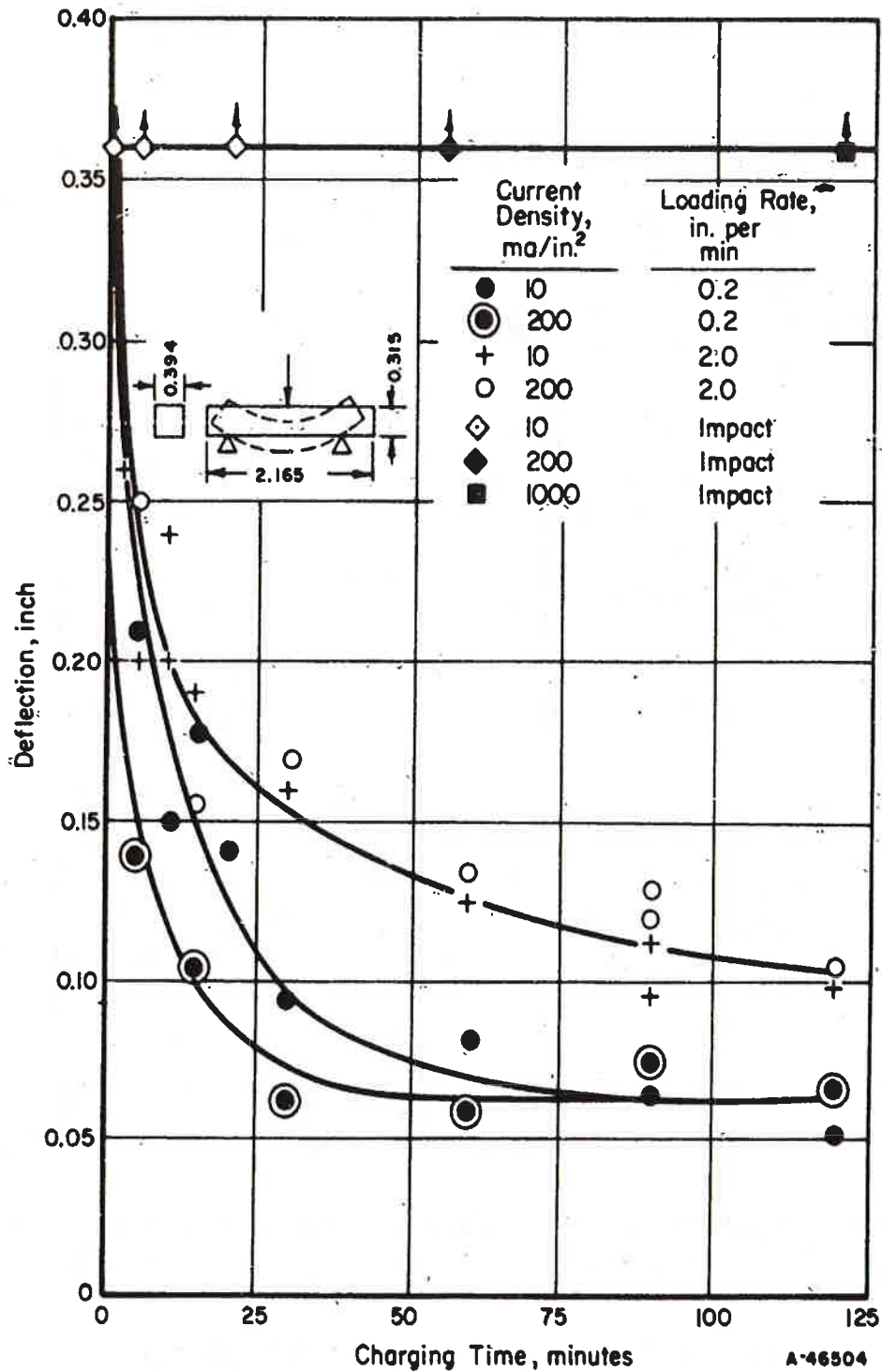


FIGURE 78. ROOM-TEMPERATURE DEFLECTION AT FRACTURE AS A FUNCTION OF ELECTROLYTIC CHARGING TIME FOR SMOOTH BEND SPECIMENS OF SAE 4340 STEEL WITH STRAIN RATE AND HYDROGEN CONTENT AS PARAMETERS⁽⁸¹⁾

Heat Treatment: Austenitized at 1600 F, oil quenched, tempered at 400 F.
Bath: 10 per cent NaOH at 30 C.

In the section of this report that describes the effect of composition, it was shown that hydrogen-induced, delayed failures are found only in body-centered-cubic steel structures, fully austenitic steels being highly resistant to embrittlement by hydrogen and apparently immune to delayed, brittle failure. A few investigations have been concerned with structures other than tempered martensite or austenite, and some of these will be reviewed here.

Various investigators showed that tensile strength is a major factor in the loss of ductility by hydrogen embrittlement. It was recognized that differences in microstructure were the underlying cause, but the relationship between the two was not understood. Hobson and Hewitt⁽¹⁾ investigated differences in microstructure in a 3 Cr-Mo steel at various levels of tensile strength, each reached by alternative heat treatments which, of course, resulted in different microstructures. They found that, with the amounts of hydrogen normally found in finished steel (about 1 to 4 cc/100 g), the effect of hydrogen on ductility at room temperature was severe only when the steel was in one of two extreme conditions of heat treatment - either hardened (martensite or bainite) and very lightly tempered or very highly spheroidized.

Bastien and Amiot⁽⁴⁶⁾ studied the delayed failure of hydrogenated plain-carbon steels that had different carbon contents and had been heat treated differently so that they differed in structure. Their results are shown in Table 17. They found that the sorbitic structure had the greatest susceptibility to hydrogen-induced, delayed, brittle failure, and globular pearlite exhibited the least susceptibility. Lamellar pearlite gave intermediate results. Sorbite, a term that is obsolete in the United States, refers to a fine mixture of ferrite and cementite, either fine pearlite or tempered martensite. Considering the strength level, their sorbite must have been tempered martensite. Their results for globular pearlite (spheroidite) appear to be inconsistent with the results of Hobson and Hewitt.

TABLE 17. INFLUENCE OF COMPOSITION AND STRUCTURE ON THE DELAYED FAILURE^(a) IN HYDROGENIZED CARBON STEELS (AFTER BASTIEN AND AMIOT)^(1,4)

Steel Designation	Carbon Content, per cent	Microstructure	Mechanical Properties, kg/mm ² (b)				
			Proportional Limit	Upper Yield Point	Tensile Strength	Lower Critical Stress	Ratio, L. C. S. / T. S.
E	0.08	Lamellar pearlite	22	24.0	37.5	21	0.56
F	0.1	Lamellar pearlite	31	35.3	44.3	30	0.68
G	0.42	Lamellar pearlite	39	41.6	60.0	39	0.65
G	0.42	Lamellar Pearlite	37	40.0	77.5	35	0.45
H	0.96	Sorbite	160	--	177.8	65	0.37
H	0.96	Globular pearlite	--	51.0	61.0	55.5	0.90

(a) Electrolytic charging began 15 hours before application of the load. L.C.S. = maximum stress which did not induce fracture of charged specimens (lower critical stress) and T.S. = tensile strength.

(b) 1 kg/mm² = 1422 psi.

It was suggested early in the studies of hydrogen embrittlement and delayed, brittle failure of high-strength steel that the decomposition of retained austenite under an applied stress in the presence of hydrogen may play a significant role. Austenite has

TABLE 18. RESULTS OF ROOM-TEMPERATURE DELAYED-FAILURE TESTS OF UNNOTCHED SPECIMENS OF SAE 4340 STEEL CATHODICALLY CHARGED WITH HYDROGEN^(a) WHILE SUBJECTED TO STATIC TENSILE STRESS⁽⁸⁾

Specimen	Applied Stress, psi	Time to Rupture, minutes
<u>Tempered Martensite, 190,000-psi UTS</u>		
A97	168,000	19.3
A94	150,000	33.3
A90	100,000	41
A95	43,000	67
A91	35,000	98
A96	35,000	113
<u>Bainite, 190,000-psi UTS</u>		
A115	>189,000 ^(b)	23.1
A111	150,000	51.5
A112	100,000	46
A113	30,000	114
A114	25,000	192
A116	20,000	312

(a) 4 per cent H₂SO₄ electrolyte with phosphorus poison; current density 8 ma/in.².

(b) Specimens A115 necked down visibly, so that the true stress at the minimum section exceeded the value of 189,000 psi based on original cross-sectional area.

Figures 2 and 13 (pages 6 and 26). As shown in Figure 13, extrapolation of the curve for the martensitic structure is consistent with the properties of the annealed, pearlitic structure which had a nominal tensile strength of 75,000 psi. These results, along with the other results for tempered martensite at several strength levels and for bainite that are included in the figures, show that structure, per se, did not have a large effect on the stress-rupture behavior of unnotched specimens during cathodic charging.

Hydrogen-induced cracks nucleate and grow much more readily in the lightly tempered martensite of a high-strength steel than in the softer pearlitic and ferritic structures. This suggested that a duplex structure consisting of a fine dispersion of a soft phase, such as ferrite, within a martensite matrix might retard the initiation and/or growth of these cracks. To produce such a dispersion, Elsea and co-workers⁽⁹⁾ austenitized several specimens in the usual manner, but isothermally transformed them at 1200 F for times varying from 5 to 30 minutes before oil quenching. These specimens were tempered to obtain an ultimate tensile strength of approximately 230,000 psi. In Table 19, the results of delayed-failure tests on these specimens are compared with the results for a completely martensitic structure tempered to the same strength level. The finely dispersed particles of ferrite had no noticeable effect on the total time delay to failure.

TABLE 19. EFFECT OF FERRITE DISPERSED IN MARTENSITE
ON RUPTURE TIME AT AN APPLIED STRESS OF
100,000 PSI^(a)(9)

Isothermal Transformation Time at 1200 F, minutes	Approximate Amount of Ferrite, per cent	Rupture Time, minutes
0	0	10.0
5	5	5.5
15	15	6.3
30	25	10.0

(a) SAE 4340 steel heat treated to the 230,000-psi strength level. Unnotched specimens cathodically charged in H_2SO_4 under standard conditions while under the static load.

Because segregations of nonmetallic inclusions have a considerable influence on the formation of cracks and hydrogen blowholes, Foryst⁽⁸²⁾ conducted an investigation to determine their effect on the sensitivity of mild steel to the action of hydrogen. Ingots were produced with various amounts of oxide inclusions, and they were processed into wire. The various materials were studied in three conditions, as follows:

- (1) Initial state (wire as produced with oxide inclusions)
- (2) Heated for 24 hours in moist hydrogen
- (3) Vacuum degassed at 800 C (1470 F).

Specimens representing the various materials and conditions were cathodically charged with hydrogen in a sulfuric acid electrolyte that contained arsenic as a cathodic poison.

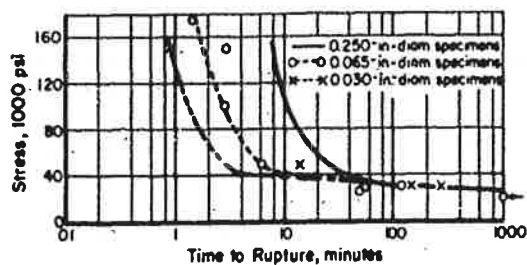


FIGURE 82. EFFECT OF SPECIMEN SIZE ON DELAYED-FAILURE CHARACTERISTICS OF AN SAE 4340 STEEL DURING CATHODIC CHARGING WITH HYDROGEN UNDER BATTELLE CONDITION A⁽⁸⁾

230,000-psi strength level.

Battelle Charging Condition A:

Electrolyte: 4 per cent by weight of H_2SO_4 in water

Poison: 5 drops per liter of cathodic poison composed of 2 g phosphorus dissolved in 40 ml CS_2

Current density: 8 ma/in.².

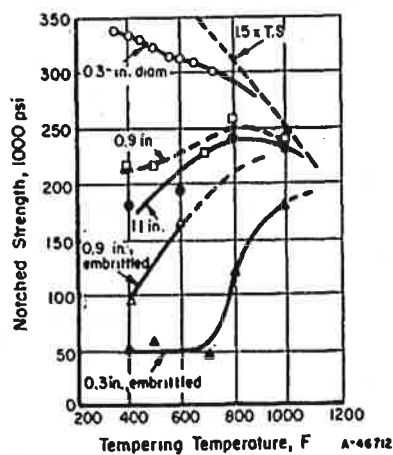


FIGURE 83. THE NOTCHED STRENGTH MEASURED FOR EMBRITTLLED AND UNEMBRITTLLED SPECIMENS OF THE INDICATED SIZES VERSUS TEMPERING TEMPERATURE⁽¹⁹⁾

The notch strength for the embrittled specimens was measured under sustained loading.

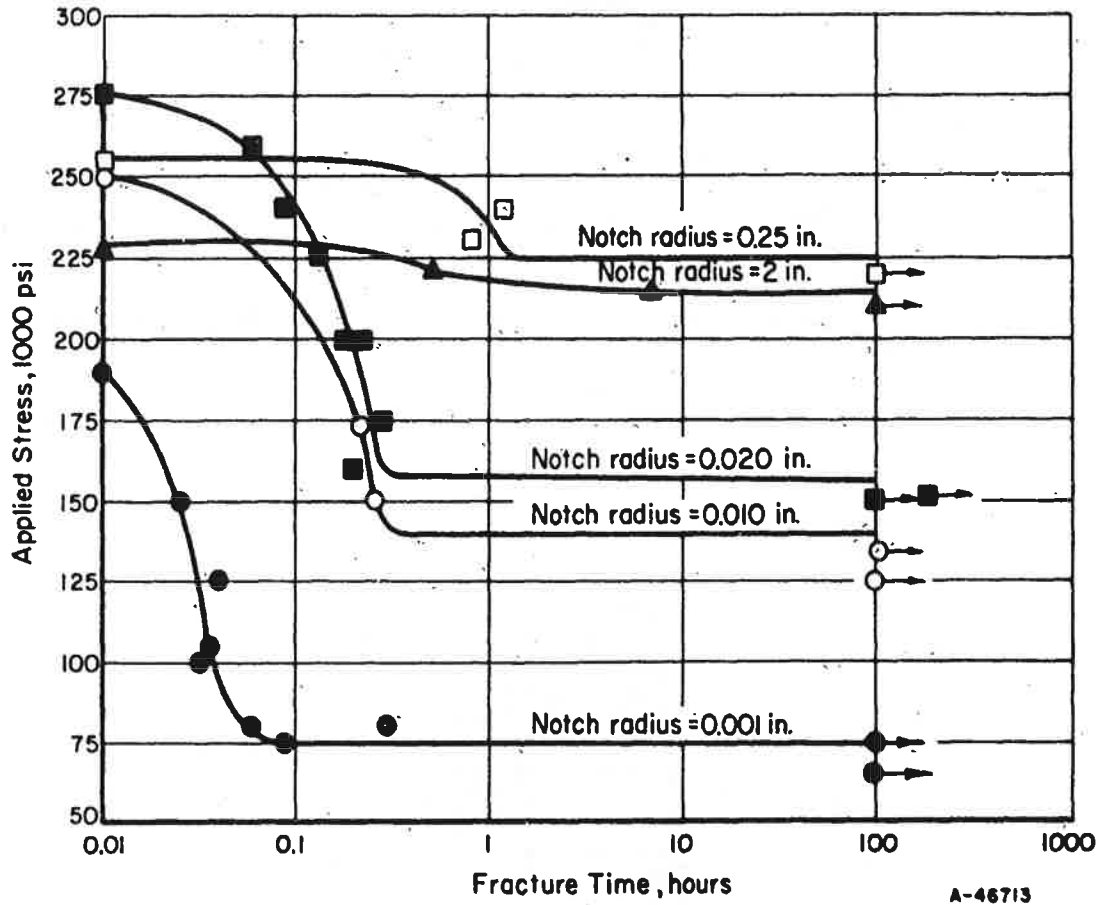


FIGURE 84. DELAYED-FAILURE CURVES FOR SPECIMENS OF DIFFERENT NOTCH SHARPNESSES⁽⁸⁵⁾

Specimens baked 0.5 hour at 300 F; 50 per cent notch; 230,000-psi strength level.

Figures 15, 86, 17 and 18 (pages 32, 118, and 33) illustrate the effect of notch acuity on the level of applied stress and time delay to failure for two steels at various strength levels⁽¹⁹⁾. The plots are based on K_t values for theoretical stress concentration. Figures 86 and 18 clearly illustrate the drastic lowering of the lower critical stress as notch sharpness was increased. Other work by these investigators⁽¹¹⁾ showed the effect of notch acuity, as well as strain rate, on the notched strength of SAE 4340 steel at various strength levels, as precharged with hydrogen under two different conditions. The results are shown in Figures 87 and 88.

EFFECT OF STRESS STATE

It has been shown in previous sections that delayed, brittle failures can be produced at low stresses in unnotched specimens subjected to uniaxial tensile loading, provided that the hydrogen content is high enough. This can be accomplished by continuous cathodic charging with hydrogen under suitable conditions. With precharged specimens, the lower critical stress usually is just a little below the short-time tensile strength of the material under this type of loading, as is shown in Figures 16 and 20 (pages 32 and 36). Numerous investigations have shown that a triaxial stress state, which is achieved by use of a notched tensile specimen, is much more conducive to the development of delayed, brittle failures in hydrogenated specimens than is uniaxial tension. This also is illustrated in the two figures just cited.

The authors are aware of no work in which the specimens were stressed in uniaxial compression. However, in some investigations, the differences between the compression and the tension surfaces of a bend specimen have been investigated. In one investigation⁽¹²⁾, the ends and three sides of smooth (unnotched) high-strength SAE 4340 specimens with a cross section 0.394 inch square were coated with Glyptal so that the hydrogen would enter only on the uncoated side during cathodic charging. After charging, the specimens were tested in a slow-bend jig with the side charged with hydrogen either in tension or compression. Figure 89a shows the effects of charging time on maximum load for specimens tested in the two orientations. The maximum load withstood by specimens with the charged side in tension decreased rapidly as the charging time was increased, whereas only a small drop in maximum load was observed when the uncharged side was tested in tension. It was noted that when the charged side was tested in tension, the depth of cleavage fracture increased with increased charging time (see Figure 89b), illustrating progressive embrittlement to deeper positions. This is added evidence that, on charging, a high concentration of hydrogen is developed initially at the surface and that a gradual penetration occurs with time.

At Battelle⁽⁸⁾, a study was made of the delayed failure of specimens statically loaded in bending and charged cathodically on the compression side while under stress. The tension side, which was exposed to the atmosphere, was notched to various depths. During cathodic charging, a hydrogen gradient was established through the specimen, with the hydrogen content being highest at the cathodically charged compression surface and lowest at the tension surface where hydrogen was escaping to the atmosphere.

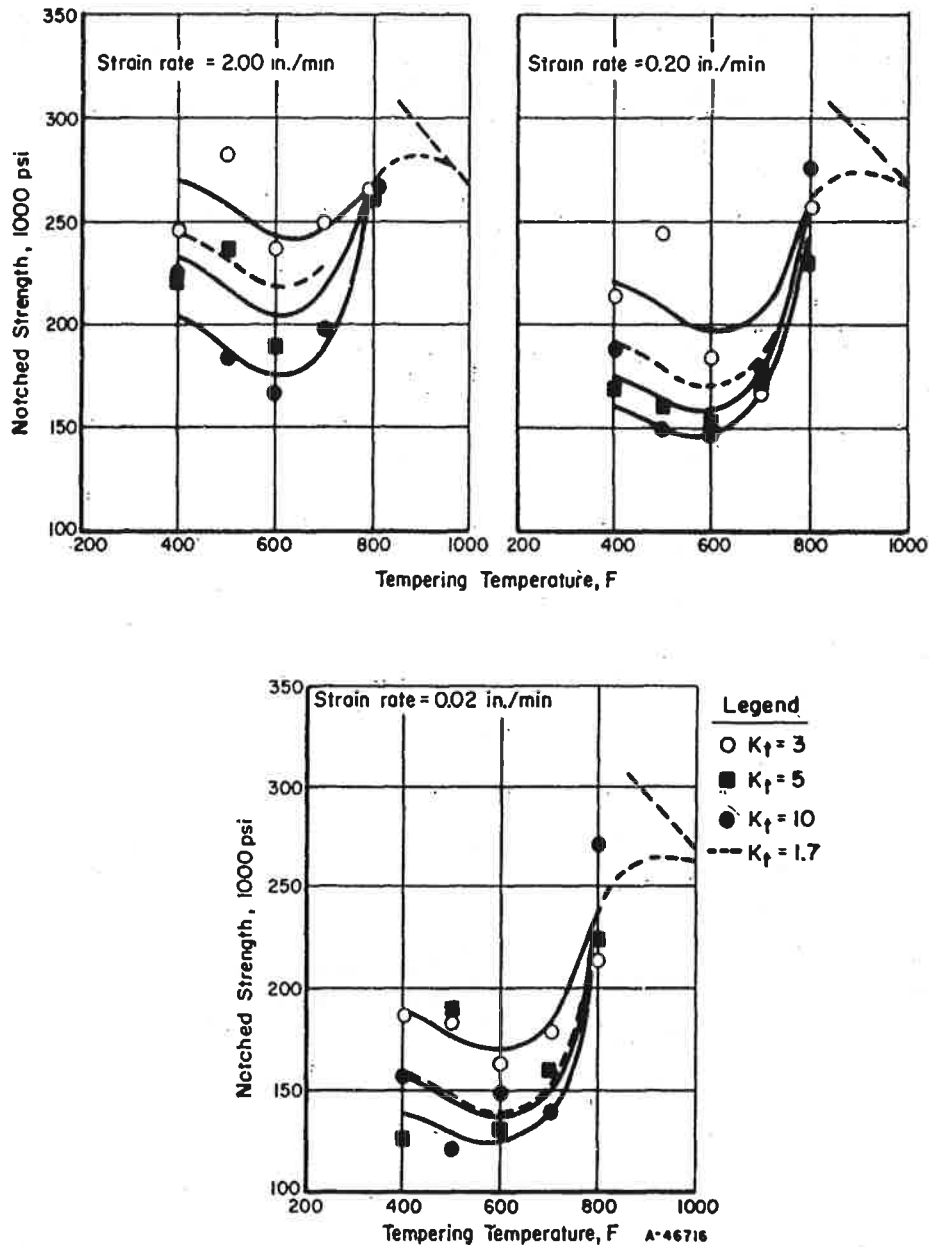


FIGURE 88. ROOM-TEMPERATURE NOTCHED STRENGTH OF 0.3-IN.-DIAM. NOTCHED TENSILE SPECIMENS OF SAE 4340 STEEL HYDROGEN EMBRITTLED BY CHARGING CONDITION C₂(11)

Charging Condition C₂:

447 ma/in.² for 2-1/2 hr;

Bath: 10% NaOH at 30 C.

Delayed failures were obtained, but none of them originated at the cathodically charged surface. The region near the cathodically charged surface behaved in a ductile manner. The results obtained are shown in Figure 26 (page 43).

Probert and Rollinson⁽²³⁾ also studied specimens that were stressed by bending and which were completely protected on all surfaces except the compressively stressed side. These specimens were found to be cracked on the tension side after cathodic treatment. Some of the results were as follows:

<u>Treatment</u>	<u>Bend Angle at Fracture, degrees</u>
Without charging	120
Charged from all sides	45
Hydrogen on tension side only	45
Hydrogen on compression side only	55

Sustained-load bend tests also were performed with hydrogen introduced on the compression side only. The following results were obtained:

<u>Sustained-Load Angle, degrees</u>	<u>Time to Failure, hours</u>
52	1
50	8
45-50	No failure

This is added evidence that the existence of compressive stress (induced by bending) in the surface being charged will not prevent hydrogen embrittlement. These investigators also showed that a compressive stress induced by shot peening will not prevent hydrogen pickup nor the embrittlement of the areas stressed in tension.

The workers at Battelle Memorial Institute⁽⁹⁾ also studied the effect of torsion loading on rupture time under sustained load. With the unnotched specimens loaded in torsion and with standard charging conditions, delayed failures were obtained as shown in Figure 90. The time for failure is plotted as a function of the principal tensile stress. The curve for the results of the standard uniaxial tension test under the same charging conditions is shown for comparison. The time for failure to occur was about the same for both the torsion test and the uniaxial tension test. The slight difference between the two curves was attributed to the error involved in loading the torsion specimens. The load, which was transmitted to the specimen by a system of pulleys, probably resulted in the actual load being slightly less than the calculated load. These data suggest that for all practical purposes the only stress that influences the delay time for failure is the maximum tensile stress.

A number of investigations have been performed in which precharged specimens have been subjected to bending stresses. Some of these have been short-time tests in which the deflection at fracture was measured. An example of the results of this type of test was given in Figure 78 (page 107). Also, delayed failures have been obtained in bend tests of precharged notched specimens and of unnotched specimens under continuous charging. However, the sustained-load tensile test of notched specimens is generally accepted as being a more sensitive and more reproducible measure of the susceptibility of hydrogenated steel to delayed, brittle failure.

in the hydrogenated condition, hydrogen was introduced into the specimens cathodically just prior to testing. The charging conditions selected were intended to be rather mild. Analyses for hydrogen content of both smooth and notched ($K_t = 8$) specimens at two different strength levels ranged between 0.4 and 0.8 ppm. Some of the results for the highest and lowest strength levels are shown in Figures 91 and 92. The S-N curves for hydrogen-embrittled material had the general appearance expected for low-cycle fatigue curves of steels heat treated to high strength levels. For the higher strength levels, the curves for smooth specimens were located entirely above those for notched specimens, while for the 210,000-psi strength level the notch-fatigue curve intersected the curve for smooth specimens at approximately 200 cycles. Between 1,000 and 10,000 cycles, the notch-fatigue strength generally was roughly one-half the smooth-fatigue strength, which was in agreement with the results of unembrittled specimens. Compared to the results for unembrittled specimens, an adverse effect of hydrogen was usually observed in the range of lowest cycles. The lone exception to this was for the smooth specimens of the 210,000-psi material, for which the fatigue strengths of embrittled and unembrittled specimens were found to be identical. In all instances, the effect of hydrogen appeared to vanish at between 1,000 and 10,000 cycles, for both smooth and notched specimens. Although the speed of these tests (250 rpm) is rather low for rotating-beam fatigue tests, it still represented a high rate of loading, namely, less than about 0.06 second from zero to maximum tension in each cycle. Thus, the loading rate for these tests was intermediate between impact and the rate used in tensile tests. The authors explained the quite small effects observed on the basis of the high rate of loading. They concluded that the normal, high-speed fatigue test is of little value as a tool for the evaluation of hydrogen embrittlement.

THEORIES OF HYDROGEN EMBRITTLEMENT

In spite of the many investigations of hydrogen embrittlement and delayed, brittle fracture reported in the technical literature, there still is no general agreement regarding the mechanism by which hydrogen reduces the ductility of steel.

A suitable theory must explain the characteristics of hydrogen embrittlement, which are quite different from those of the more conventional forms of embrittlement. Hydrogen embrittlement disappears at low and high test temperatures and, therefore, is most severe in an intermediate temperature range, usually in the vicinity of room temperature. Also, hydrogen embrittlement is inversely related to the strain rate, which is just the reverse of most other forms of embrittlement.

One of the unique characteristics of delayed, brittle failure induced by hydrogen is that there is a lower critical stress below which failure will not occur. Different investigations showed quite early that the hydrogen-induced, delayed, brittle failure process occurs in three distinct stages:

- (1) The incubation period
- (2) A period of relatively slow crack growth, or crack propagation
- (3) Sudden rupture with extremely rapid crack growth through the central core essentially free of hydrogen.

In subsequent work, crack initiation and propagation were studied in detail, and it was found that crack propagation is a discontinuous process which consists of a series of separate crack initiations and propagations. The average hydrogen concentration is not sufficient to propagate a crack. Thus, crack propagation cannot occur until the hydrogen concentration increases in a localized region in front of the crack. This increase occurs through hydrogen diffusion, which is induced either by a stress gradient or a hydrogen gradient. Both the incubation period and crack-propagation phase are controlled and paced by the diffusion of hydrogen. Thus, above a particular threshold stress, the conditions necessary for localized cracking are dependent essentially only on the development of a critical hydrogen content. Crack initiation and crack growth have been discussed previously in other sections of this report, particularly in the sections dealing with the effects of various hydrogen concentrations and the movement of hydrogen. For further information, the reader is referred to some of the more recent papers discussing these aspects of the hydrogen problem; these include References 49, 80, and 87.

Because delayed failure consists of a series of many individual crack initiations, the factors that determine the incubation time are particularly important in explaining the delayed-failure mechanism. In Reference 87, it is suggested that the initiation of a hydrogen-induced crack is dependent on two factors, as follows:

- (1) The stress-induced diffusion of hydrogen that produces an appreciable build up of hydrogen in a localized region
- (2) The basic effect of hydrogen on the material that causes localized failure, that is, a crack.

The first factor has been dealt with at some length in preceding sections. The second factor, the ability of hydrogen to lower the fracture stress, has been the main part of several of the more recent theories proposed to explain hydrogen embrittlement. Most investigators have concluded that the hydrogen pressure in certain voids or imperfections which act as the fracture embryos tends to lower the applied stress at which these embryo fractures become active. Each of the theories advanced to explain hydrogen embrittlement depends on a critical combination of hydrogen and stress. Therefore, they can be applied to a certain extent to the delayed-failure process also. However, most of them do not explain the observed insensitivity of the incubation time to variations in applied stress.

Except for Troiano's theory⁽⁸⁸⁾, most of the newer theories involve the surface adsorption of hydrogen through the precipitation of hydrogen gas on the surface of a crack or lattice imperfection, and this adsorption is seen as lowering the surface energy necessary for the extension of the crack.

Troiano, who has studied the delayed-failure process at great length, believes the implication is strong that delayed failure is the result of a lowering of the true fracture strength of the iron lattice which results from the segregation of interstitial hydrogen atoms in the lattice at the region of maximum triaxiality near the tip of the crack.

The theories advanced to explain the phenomena of hydrogen embrittlement and delayed, brittle failure of high-strength may be arranged in four groups.

The first theory was the planar-pressure theory of Zapffe and co-workers. They assumed that molecular hydrogen precipitates in internal voids of the crystal structure

Thus, hydrogen embrittlement becomes nothing other than a phenomenon of internal precipitation along imperfectly disposed crystallographic planes much as in "age hardening", except that here the precipitate is a gas and, therefore, causes no hardening. Even in an unstrained crystal, molecular hydrogen collects in the planar separations which already exist as an inherent feature. The metal becomes embrittled when the gas pressure exceeds some critical value approximating the elastic strength of the crystal. On testing, however, the plastic movement opens the imperfections further, which logically reduces the pressure of molecular hydrogen within the voids to values which may be less than the critical. At the high pressures associated with embrittlement, an appreciable reserve of hydrogen atoms must lie within the adjoining lattice under conditions of quasi-equilibrium, as expressed by $[H] = K \cdot (P_{H_2})^{1/2}$. Reduction of P_{H_2} in the lattice void then causes further precipitation of those hydrogen atoms. If the rate of strain is not too rapid, precipitation will replenish P_{H_2} sufficiently rapidly to maintain the embrittled condition. If the rate of strain is increased, however, until the rate of decrease in P_{H_2} exceeds the rate of restoration through further precipitation of hydrogen, the apparent embrittlement should decrease, as is observed. The effect of temperature has an obviously similar relationship, since the pressure of a gas phase likewise decreases with decreasing temperature. Thus, there will be a critical temperature, also a critical rate of cooling, for any given set of conditions, such that the critical embrittlement pressure P_{H_2} is decreased more rapidly than it is replenished by precipitating hydrogen, and embrittlement will decrease, as is observed experimentally.

Bastien and Azou⁽⁹³⁾ proposed that hydrogen is concentrated around dislocations which discharge it into the voids during plastic straining. With this build up of molecular hydrogen in the voids, an increase of pressure occurs which causes embrittlement by raising triaxial stresses around the voids.

According to De Kazinczy^(94, 43), hydrogen embrittlement is caused by a lowering of the shear strength and the cleavage strength. He explains this by assuming that molecular hydrogen of high pressure is included in a Griffith crack or some other crack which initiates fracturing. The energy necessary to open a crack and cause it to grow is assumed to arise from the expansion of the hydrogen gas and release of energy during crack growth, which results in a lowering of the fracture stress. It is shown that hydrogen diffusion into the crack is needed during crack spreading, and this diffusion explains the time and temperature effects of hydrogen embrittlement.

These results have been correlated with the diffusion of hydrogen by Toh and Baldwin⁽⁷⁸⁾ (see Figure 63, page 95).

One of the most characteristic features of hydrogen-induced failure in high-strength steels is the delay-time effect for failure to occur under the action of static loads. In 1952, Petch and Stables⁽⁷²⁾ published the first plausible explanation of this time-delay behavior which they predicted and which was soon observed experimentally by a number of investigators. Their proposed mechanism for delayed fracture was based on the Griffith mechanism for the fracture of completely brittle materials. They proposed a suitable modified-form of the Griffith-Orowan⁽⁹⁵⁾ theory of static fatigue in glass. This theory requires the development of a suitable crack which, through reduction in the cross section, leads to eventual overloading of the remaining uncracked cross section and, thus, failure. Petch and Stables explain the delay feature of the fracture

- (2) Sufficient mobility of the hydrogen to allow the phenomenon to be observed in a reasonable period of time under the chosen test conditions.
- (3) A material with a sufficiently high yield strength, in order that a critical interaction energy between local stress fields and the hydrogen may be attained.

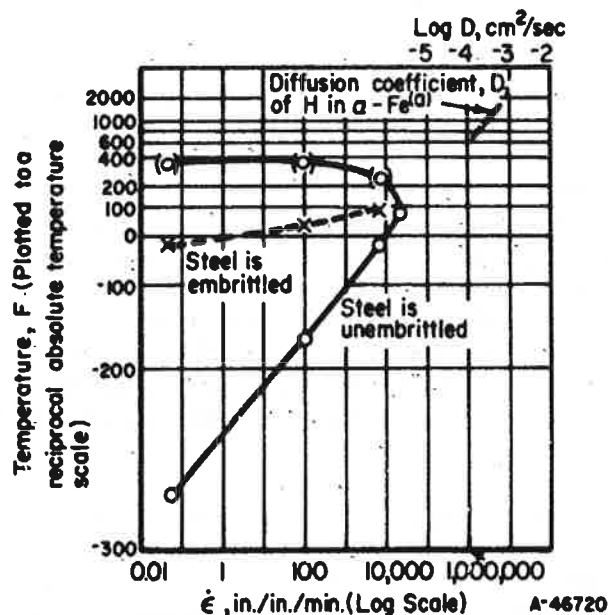


FIGURE 93. A PLOT OF TEMPERATURES AT WHICH DUCTILITY OF CHARGED STEELS RETURNS TO THE DUCTILITY CURVE OF UNCHARGED STEELS AS A FUNCTION OF STRAIN RATE (CIRCLES)⁽⁷⁷⁾.

The crosses indicate the combinations of temperature and strain rate at which a minimum in the ductility curves occurred. The diffusion coefficient of hydrogen in α iron is plotted to the upper scale.

Note that the reciprocal absolute temperature scale is inverted.

(a) Geller, W., and Sun, Tak-Ho, *Archiv. Eisenhüttenwesen*, 21, 423-430 (1950).

Based on the results they obtained by prestraining-and-aging experiments on hydrogenated high-strength steel, Morlet, Johnson, and Troiano^(44, 97) concluded that the hydrogen concentration in the triaxial region in front of a void or large imperfection, rather than the pressure within the void, is the determining factor for embrittlement. This mechanism to explain the nature of crack kinetics of the delayed failure is based on the stress-induced diffusion of hydrogen to the area of maximum triaxiality. When the hydrogen concentration in this region reaches a critical value, a crack is nucleated. This initial crack propagates instantaneously until it is stopped, presumably by some degree of plastic flow or by the higher fracture stress of the adjacent material outside the region of maximum triaxiality. For cracking to resume, hydrogen must diffuse to

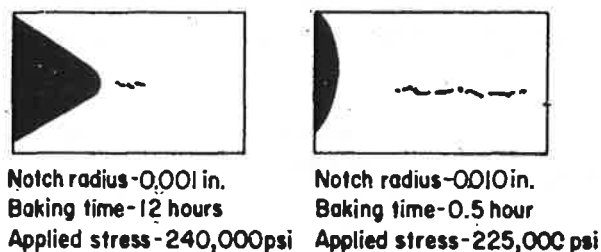


FIGURE 94. CRACKS OBSERVED IN NOTCHED SPECIMENS SECTIONED AFTER STATIC LOADING⁽⁴⁹⁾

Specimens were hydrogenated, cadmium-plated, and baked at 300 F. Longitudinal sections at 100X; reduced approximately 50 per cent for reproduction.

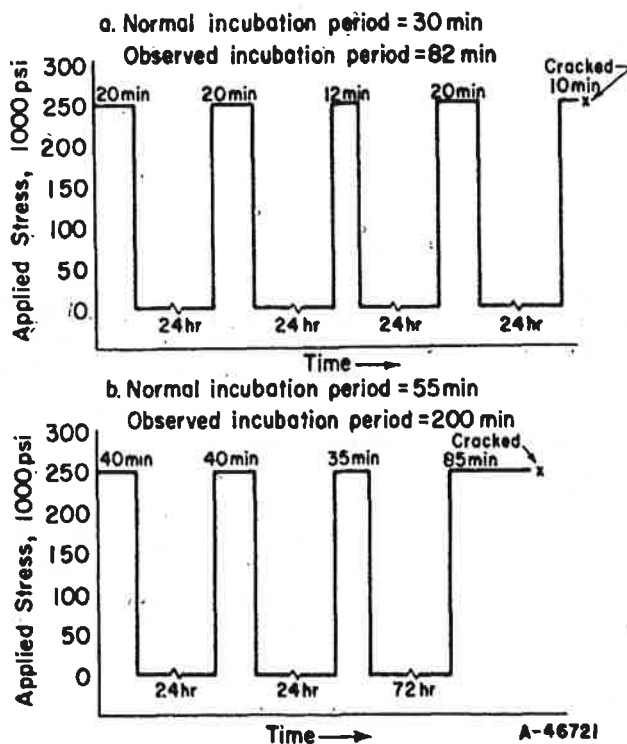


FIGURE 95. SCHEMATIC REPRESENTATION OF LOADING AND AGING TREATMENTS WHICH PRODUCE INCUBATION PERIODS MUCH LONGER THAN NORMAL INCUBATION PERIODS FOR THESE HYDROGEN CONCENTRATIONS⁽⁴⁹⁾

Sharp-notch specimens, 230,000-psi strength level.

tensile test conducted at room temperature, because it is necessary to measure the hydrogen content. Hence, the tests were conducted in liquid nitrogen (-321 F), at which temperature diffusion during the test that might alter the local hydrogen content would be nil. A series of unnotched SAE 4340 tensile specimens heat treated to the 230,000-psi strength level were electrolytically precharged with hydrogen for 24 hours in a poisoned 4 per cent sulfuric acid solution. The hydrogen content was varied over a considerable range by adjusting the charging current. A linear relation was obtained between the hydrogen content and the log of the current density over a range of current densities, just as had been reported by other investigators. The point where the hydrogen content as a function of charging current deviated from linearity for a fixed charging time (8 ppm in this experiment) corresponded to local failure by cracking or blistering and the start of irreversible embrittlement.

Tensile tests were conducted at -321 F, and reduction in area was used to indicate the degree of embrittlement. Figure 96 shows the effect of hydrogen content (indicated by the current density) on the ductility of the high-strength steel at -321 F. The results show that the relationship between hydrogen and stress necessary to initiate a crack depends primarily on the hydrogen content. At these low temperatures, where diffusion of hydrogen was nil, no embrittlement occurred for hydrogen contents below about 5 ppm. However, when this critical hydrogen content was reached, catastrophic embrittlement took place. Inasmuch as the basic nature of delayed failure is not markedly affected by temperature, it was concluded that the initiation of a crack at room temperature also would be dependent on the development of a critical hydrogen content. It therefore was concluded that once above some threshold value, the stress in the delayed-failure process merely serves to produce sufficient hydrogen grouping (called stress-induced diffusion) to initiate a crack in the region where a fracture embryo exists.

Troiano and co-workers went through a theoretical treatment of the role of stress-induced diffusion, considering such factors as the number of hydrogen atoms arriving at the point of maximum binding energy in a given time, the distortion of the lattice due to hydrogen, the elastic constants, test temperature, the particular notch geometry, and the applied stress. They concluded that, in order for embrittlement (that is, local crack initiation) to occur, the number of hydrogen atoms arriving at the point of maximum binding energy in a given time (which would now correspond to the incubation time) must equal the critical hydrogen content. Therefore, for a given temperature and notch geometry, the following simplified relationship applies:

$$p_i \cdot t_i = \text{constant},$$

where t_i is the incubation time corresponding to an applied stress of p_i . On this basis, the incubation time as a function of applied stress can be calculated using only one experimental point to evaluate the constant for a given temperature and notch geometry. Figure 97 presents a comparison of the relationship between stress and time as determined by the above equation and by experiment. The slopes of the predicted curves agree reasonably well with the results obtained experimentally.

Each of the various theories of hydrogen embrittlement depends on a critical combination of hydrogen and stress, and each also depends in some way on the calculated pressure developed by the hydrogen in a certain type of void or imperfection. As was seen above, the mechanisms proposed by Zapffe, De Kazinczy, Bastien and Azou, and Petch and Stables depend directly on the pressure in an imperfection. In the concept of

embrittlement presented by Troiano and his co-workers, the hydrogen pressure in the void influences the embrittlement by regulating the hydrogen content in the lattice in the triaxial region adjacent to the void. Recently Bilby and Hewitt(99) published the first results of an incomplete study of the stability of a wedge-shaped microcrack under constant external stress and internal pressure. Their results suggested that only a very small quantity of lattice-dissolved hydrogen is required to exert an embrittling effect directly through pressure in wedge cracks. A number of methods have been used to calculate the relationship between hydrogen content and pressure in a void, and several give essentially the same results - for example, the methods in References 43 and 32. Using the method of De Kazinczy(43), Steigerwald et al.(87) calculated the pressure for a steel with 0.008 per cent voids; the results they obtained are plotted in Figure 98. These results indicate that the calculated pressure rises extremely rapidly over a very narrow range of hydrogen contents. The calculated relationship between pressure and hydrogen content (Figure 98) is similar to that obtained experimentally between stress and hydrogen content (based on the results in Figure 96). In agreement with the postulated mechanisms, these results indicate qualitatively that the hydrogen pressure in a void is the critical parameter influencing embrittlement. However, the exact mechanism by which hydrogen lowers the fracture stress, thus causing embrittlement, still is not understood.

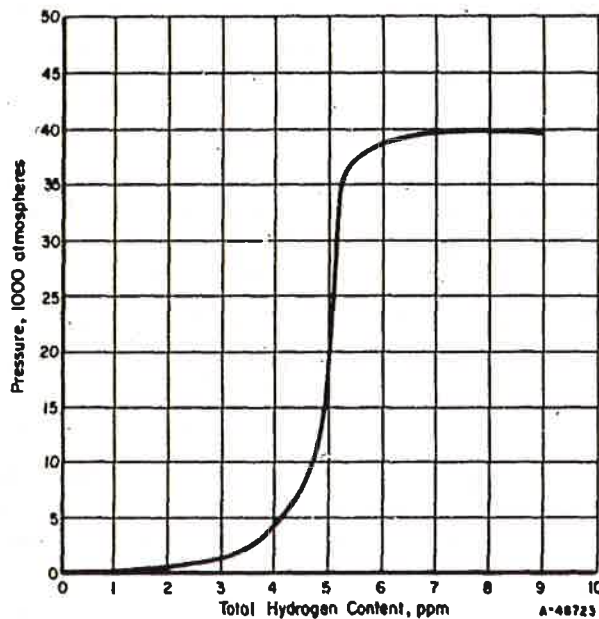


FIGURE 98. RELATIONSHIP BETWEEN PRESSURE AND HYDROGEN CONTENT CALCULATED BY METHOD OF DE KAZINCZY (REFERENCE 43) FOR STEEL WITH 0.008 PER CENT VOIDS(87)

Temperature = -321 F

Garofalo, Chou, and Ambegaokar(100) recently considered the combined effects of pressure and adsorption, using current ideas on the dislocation theory of fracture. This work is rather similar to that of Bilby and Hewitt(99), but the two analyses appear to differ in certain important respects and suggest rather different conclusions.

(850-950 F). The characteristics of the failures were similar to those obtained with hydrogenated high-strength steel at ambient temperatures. The almost perfect correspondence of the behavior of the two systems led to the conclusion that the same mechanism was operative in both cases. This mechanism is based on the idea of a local lowering of the cohesive strength of the lattice due to an accumulation of interstitial solute atoms in regions of high elastic strains. Thus, these appear to have been carbon-induced, delayed, brittle failures. The elevated temperature was required so that carbon would have sufficient mobility to move in response to the stress gradient. This paper restates their proposed mechanism for hydrogen-induced, delayed, brittle failure.

TESTS FOR HYDROGEN EMBRITTLEMENT

The purpose of this section is to discuss tests that can be used to determine if a hydrogen-embrittlement problem, and specifically a delayed-brittle-failure problem, exists. Most of these tests depend on a comparison of the properties of a material carefully processed so as to have a minimum hydrogen content with those of a material processed under suspect conditions.

For careful processing, the heat-treating atmosphere should not be conducive to hydrogen pickup from the steam reaction, so the water vapor content should be relatively low. Also, the partial pressure of hydrogen should be low. (Treatment at elevated temperatures in a wet hydrogen atmosphere is one method that is used to intentionally introduce hydrogen into steel.) A dry argon atmosphere is ideal for use in laboratory investigations, but often this is not practicable in the plant. No acid pickling, cathodic cleaning, nor electroplating operations are permissible, as these operations usually introduce hydrogen into the steel.

In some laboratory investigations, in order to obtain a uniform base material and minimize variations in hydrogen content resulting from steelmaking operations, a procedure has been adopted to reduce the hydrogen content of the steel as much as possible. To accomplish this, the steel is austenitized at a suitable temperature and furnace cooled to a temperature in the pearlite-formation range where complete isothermal transformation can be achieved on holding for a reasonable time (a few hours), allowing ample margin for heat-to-heat variations in transformation time. Then the temperature is lowered to approximately 500 F, and the material is held for an additional time of perhaps 24 hours to achieve the lower equilibrium solubility associated with the lower temperature. After rough machining of test specimens, the specimens are heated for hardening by austenitizing in a dry argon atmosphere. They are quenched and tempered in the usual fashion.

Suspect treatments include acid pickling, cathodic cleaning, electroplating, electrochemical machining, heating in moist atmospheres or hydrogen-bearing atmospheres, exposure of steel to moisture sufficient to cause corrosion (including the use of water for pressure testing of pressure vessels), and exposure to hydrogen at elevated temperatures and pressures. Also, especially for heavy sections, hydrogen introduced in the steelmaking operations may be a factor unless suitable vacuum processing has been used to minimize hydrogen pickup from these sources. However, in the aircraft and

was clearly demonstrated in work of Frohmberg et al. (5) and Klier, Muvdi, and Sachs (19) in which variations in notch acuity were studied. This work has been described in the section dealing with the effect of notch acuity. Figures 20, 86, and 18 (pages 36, 118, and 33, respectively) clearly show the effect.

The sustained-load test of cadmium-plated notched specimens has seen wide use as an indicator of hydrogen embrittlement that occurs as the result of hydrogen introduced into high-strength steel by cleaning and electroplating operations. The reason for this is that the plots of applied stress versus failure time in the sustained-load test are strongly influenced by the quantity of hydrogen present. If all other variables are held constant, the lower critical stress (the stress level below which failure is not obtained) has been shown to increase with decreasing levels of hydrogen. Some of the other variables that affect the lower critical stress at room temperature are the strength level of the material, notch acuity or stress-concentration factor, and eccentricity of loading during testing.

No reports are known of failures in compression, and failures have not initiated in the compression side of bend specimens, as was discussed in the section that deals with the effects of different stress states. The rotating-beam fatigue test was studied by Sachs' group (86). They concluded that, as a tool for the evaluation of hydrogen embrittlement, the normal high-speed fatigue test is of little value. Also, the high cost of specimen preparation makes the test uneconomical. However, in a study of inhibitors for hydrogen pickup during acid pickling at Aberdeen Proving Ground, as discussed by Dauerman (106), embrittlement was measured with the Moore fatigue test. Other experimental work on specimens loaded in torsion showed that the failure times were not influenced by the state of the stress and, for all practical purposes, the only stress that influenced the delay time for failure was the maximum tensile stress (9). The plane of the cracks in torsion specimens was normal to the maximum tensile stress.

As a result of these various tests, it is apparent that the most sensitive test for revealing hydrogen embrittlement and the most satisfactory way to study delayed, brittle failures is the static-loading test. Under carefully controlled conditions, this sustained-load test of notched tensile specimens is a satisfactory indicator of susceptibility to delayed, brittle failure. However, this test involves a stress-rupture machine of some sort, and care must be taken to secure good alignment of specimen axis and grips so as to attain virtually uniaxial tensile loading, with bending stresses at a minimum. Therefore, there has been considerable effort to develop other tests.

Figure 99 shows a static-loading device that can be used in place of more expensive stress-rupture machines. The load is measured by means of strain gages attached to a reduced section of the loading screw. Belleville springs are provided to reduce the effect of any relaxation of the specimen or apparatus. This device has been used with precharged specimens, and, with the electrolytic cell in place as shown in the figure, it is suitable for continuous charging while under load. The slight decrease in the indicated stress during the test is considerably less than the probable error in loading. The Gregg tension ring is a small and simple device for applying and maintaining a tensile load on a notched stress-rupture specimen. The load is applied to the test specimen through an elastic ring and is measured by the change in diameter of the ring. The static bend test is favored by some investigators, and others use a constant-rate bend test to detect embrittlement but not susceptibility to delayed failures. References 81 and 107 describe a constant-rate bend test, and results obtained with it are compared with those from other tests. For sustained loading, a notched C-ring (the specimen) stressed by a hollow bolt, the load upon which is detected by a strain gage, has

been devised(108, 109, 110). Jones(111) has described a test in which a long slender column is bent by loading in compression. Other devices and test methods are described in References 112, 113, and 114. A recent article has suggested that neutrons may soon be used as a nondestructive test to locate hydrogen in metals(115).

A survey in 1957 of 25 companies concerned with hydrogen embrittlement of ferrous metals used in aircraft and missiles showed the need for standardizing the engineering test methods for detecting hydrogen embrittlement. Methods then in use included the standard tensile test, the notched tensile test, either of these two types of tensile test in conjunction with a sustained load test, seven types of bend tests, and sustained-load tests of notched or smooth tensile bars, torqued bolts, flat bars, round rings, and C-rings. The Aerospace Research and Testing Committee set up Project W-95 to select or develop a standard test, preferably a short-term test, that would give an accurate indication of the degree of hydrogen embrittlement in ferrous materials. In this project, six basic methods of testing for hydrogen embrittlement were investigated. They were the tensile test, stressed-ring test, sustained-load notched tensile test, constant-rate bend test, torqued-bolt test, and static-bend test. Modifications of the test specimen and procedures brought the total number of methods investigated to 12. Of all the methods investigated, the sustained-load notched tensile test was found to be the most sensitive and reproducible. However, two versions of this test were used (the chief difference being in the root radius of the notch), and they showed considerable difference in time to failure for specimens embrittled under identical conditions by the same laboratory. Therefore, further work was recommended to arrive at a standard sustained-load notched tensile test. This work is described in detail in Reference 116.

In a recent paper, Johnson(117) has discussed a method for detecting hydrogen embrittlement resulting from electrolytic cadmium plating. Sustained-load tests were performed with specimens having notch root radii of 0.001, 0.003, 0.005, and 0.025 inch. The three sharper notches all indicated good sensitivity to high degrees of embrittlement. For low degrees of embrittlement, it was concluded that the notch root radius should be 0.003 inch or smaller for maximum sensitivity.

CONCLUSIONS:

(1) Composition is not an important factor in the hydrogen-induced, delayed, brittle failure of steels. No alloying element, either substitutional or interstitial, has eliminated the tendency for hydrogen-induced, delayed, brittle failure, and none has been truly effective in retarding failures of this type. All ferritic and martensitic steels studied have been susceptible to this type of failure when tested under appropriate conditions. No instance of hydrogen-induced failure of a completely austenitic steel is known. However, with very severe charging conditions, austenitic steels can suffer some loss in ductility. The resistance of austenitic steels to this type of failure appears to be related to the face-centered-cubic structure.

(2) Under practicable conditions of processing steel, the strength level appears to be the most important factor governing the occurrence of delayed, brittle failure. As the nominal tensile strength of the steel is increased, both the minimum applied stress for failure and the time required to produce failure decrease. Thus, high-strength steel

is more severe in a notched tensile specimen with the triaxial stresses introduced by the notch. The most sensitive test for hydrogen embrittlement and delayed, brittle failure is the static-loading test of a notched specimen.

(7) In steels, hydrogen-induced, delayed, brittle failures are found only in body-centered cubic microstructures; fully austenitic steels are quite resistant to hydrogen embrittlement. Tempered martensite, bainite, lamellar pearlite, and spheroidized structures all are susceptible to hydrogen embrittlement, and delayed failures occur in all four. It has been established that the transformation of retained austenite is not a primary cause of these failures. Structure per se appears to be relatively unimportant so long as it is body-centered cubic. Rather, the ultimate tensile strength of the material, regardless of structure, is the chief factor influencing delayed, brittle failures.

(8) The section size also is a factor, at least in instances where the hydrogen is initially concentrated at the surface, as it is shortly after electroplating, pickling, or electrolytic charging, or when hydrogen is introduced electrolytically or by corrosive attack while the part is under sustained load. Increased section size results in longer delays before brittle failure. In addition, section size has a marked influence on the recovery of properties by aging to remove hydrogen from the steel; hydrogen removal from large masses is very slow.

(9) Because the delayed, brittle failure induced in steel by hydrogen is a low-strain-rate phenomenon, it is relatively easy to study crack initiation and propagation. Acoustical, electrical resistance, and metallographic methods have been used in these studies; they have shown that the delayed-brittle-failure process consists of the following three stages:

- (1) Incubation
- (2) A period of slow crack growth (propagation)
- (3) Sudden rupture through the central core that frequently is essentially free of hydrogen.

Crack propagation has been shown to be a discontinuous process that consists of a series of separate crack initiations and propagations. Both the incubation period and crack propagation are controlled by the diffusion of hydrogen. Above a certain threshold stress, the conditions necessary for localized cracking depend almost entirely on the development of a critical hydrogen content. This level of hydrogen is built up by diffusion, induced either by a hydrogen gradient or by a stress gradient. However, there still is no general agreement regarding the mechanism by which hydrogen reduces the ductility of steel and lowers its load-carrying ability. Several theories of hydrogen embrittlement have been proposed. Each of them depends on a critical combination of stress and hydrogen, and each depends in some way on the development of a hydrogen pressure in a certain type of void or imperfection.

- (13) Gasior, E., and Prajsnar, T., Private communication to M. Smialowski in 1959 and described by him on page 241 in his book Hydrogen in Steel, Pergamon Press (1962).
- (14) Smialowski, Michael, Hydrogen in Steel, Pergamon Press, New York (1962), pp 239, 241.
- (15) Johnson, H. H., Johnson, R. D., Frohmberg, R. P., and Troiano, A. R., "Static Fatigue in Twelve Heats of 4340 Steel Embrittled with Hydrogen", WADC TN 55-306 (August, 1955).
- (16) Blanchard, P., and Troiano, A. R., "Delayed Failure and Notch Tensile Properties of a Vacuum Melted 4340 Steel", WADC TN 58-176 (September, 1958).
- (17) Raring, R. H., and Rinebolt, J. A., "Static Fatigue of High-Strength Steel", NRL Memorandum Report 452 (April, 1955).
- (18) Raring, R. H., and Rinebolt, J. A., "Static Fatigue of High Strength Steel", Trans. Am. Soc. for Metals, 48, 198-212 (1956).
- (19) Klier, E. P., Muvdi, B. B., and Sachs, G., "The Response of High-Strength Steels in the Range of 180,000 to 300,000 psi to Hydrogen Embrittlement From Cadmium-Electroplating", Am. Soc. Testing Materials, Proceedings, 58, 597-619 (1958).
- (20) Klier, E. P., Muvdi, B. B., and Sachs, G., "Design Properties of High-Strength Steels in the Presence of Stress Concentrations and Hydrogen Embrittlement. Part 3. The Response of High-Strength Steels in the Range of 180,000-300,000 psi to Hydrogen Embrittlement From Cadmium Electroplating", WADC TR 56-395, Part 3 (March, 1957).
- (21) Srawley, J. E., "Hydrogen-Embrittlement Susceptibility of Some Steels and Nonferrous Alloys", NRL Report No. 5392 (October 19, 1959).
- (22) Geyer, N. M., Lawless, G. W., and Cohen, B., "A New Look at the Hydrogen Embrittlement of Cadmium Coated High Strength Steels", WADC TR 58-481 (December, 1958).
- (23) Probert, L. E., and Rollinson, J. J., "Hydrogen Embrittlement of High Tensile Steels During Chemical and Electrochemical Processing", Electroplating and Metal Finishing, 14, 323-326, 342 (September, 1961); 356-360, 382 (October, 1961); 396-401, 406 (November, 1961); 15; 6-9 (January, 1962).
- (24) Beachum, E. R., Johnson, H. H., and Stout, R. D., "Hydrogen and Delayed Cracking in Steel Weldments", Welding J., 40 (4), 155-s - 159-s (April, 1961).
- (25) Schuetz, A., and Robertson, W., "Hydrogen Absorption, Embrittlement and Fracture of Steel", Corrosion, 13, 437t-458t (1957).

- (41) Steigerwald, E. A., Schaller, F. W., and Troiano, A. R., "The Role of Stress in Hydrogen Induced Delayed Failure", *Trans. Met. Soc. AIME*, 218, 832-841 (October, 1960).
- (42) Hobson, J. D., and Sykes, C., "Effect of Hydrogen on the Properties of Low Alloy Steels", *J. Iron and Steel Inst.*, 169, 209-220 (1951).
- (43) De Kazinczy, F., "A Theory of Hydrogen Embrittlement", *J. Iron and Steel Inst.*, 177, 85-92 (1954).
- (44) Morlet, J. G., Johnson, H. H., and Troiano, A. R., "A New Concept of Hydrogen Embrittlement in Steel", WADC TR 57-190 (March, 1957).
- (45) Johnson, R. D., Johnson, H. H., Morlet, J. G., and Troiano, A. R., "Effects of Physical Variables on Delayed Failure in Steel", WADC TR 56-220 (June, 1956).
- (46) Bastien, Paul, and Amiot, Pierre, "The Influence of Hydrogen in Steel on the Phenomenon of Delayed Fracture", *Compt. Rend.*, 241, 1760-1762 (1955), In French.
- (47) Bucknall, E. H., Nicholls, W., and Toft, L. H., "Delayed Cracking in Hardened Alloy Steel Plates", *Symposium on Internal Stresses in Metals and Alloys*, Monograph and Report Series No. 5, Institute of Metals, 351-365 (1948).
- (48) Bell, W. A., and Sully, A. H., "Some Effects of Hydrogen on the Delayed Fracture of High-Tensile Steel", *J. Iron and Steel Inst.*, 178, 15-18 (1954).
- (49) Johnson, H. H., Morlet, J. G., and Troiano, A. R., "Hydrogen, Crack Initiation, and Delayed Failure in Steel", *Trans. Met. Soc. AIME*, 212 (4), 528-536 (August, 1958).
- (50) Darken, L. S., and Smith, R. P., "Behavior of Steel During and After Immersion in Acid", *Corrosion*, 5, 1-16 (1949).
- (51) Bardenheuer, P., and Ploum, H., "The Hydrogen Embrittlement of Steel in Dependence on the Amount of Absorbed Hydrogen", *Mitt. Kaiser-Wilhelm Inst. Eisenforschung*, 16, 137-140 (1934), In German.
- (52) Sims, C. E., Moore, G. A., and Williams, D. W., "The Effect of Hydrogen on the Ductility of Cast Steels", *Trans. Am. Inst. Mining Met. Engrs.*, 176, 283 (1948).
- (53) Sims, C. E., "Hydrogen Elimination by Aging", *Trans. Am. Inst. Mining Met. Engrs.*, 188, 1321 (1950); *J. Metals*, 188 (11), 1321 (November, 1950).
- (54) Zapffe, C. A., and Haslem, M. E., "Measurement of Embrittlement During Chromium and Cadmium Electroplating and the Nature of Recovery of Plated Articles", *Trans. Am. Soc. Metals*, 39, 241-258 (1947).
- (55) Zapffe, C. A., and Haslem, M. E., "Hydrogen Embrittlement in Cadmium and Zinc Electroplating", *Plating*, 37, 366-371 (April, 1950).

- (69) Spaeth, C. E., "Defects, Surface Finishes, and Hydrogen Embrittlement", Mechanical and Metallurgical Behavior of Sheet Materials, Proc. 7th Sagamore Ordnance Materials Research Conf., Racquette Lake, N. Y., pp III-11 to III-37, August 16-19, 1960.
- (70) Norton, Francis J., "Diffusion of D₂ from D₂O Through Steel", J. Appl. Phys., 24, 499 (1953).
- (71) Steigerwald, E. A., "Delayed Failure of High-Strength Steel in Liquid Environments", Proc. Am. Soc. Testing Materials, 60, 750-760 (1960).
- (72) Petch, N. J., and Stables, P., "Delayed Fracture of Metals Under Static Load", Nature, 169, 842-843 (May 17, 1952).
- (73) Davis, Robert A., "Stress Corrosion Investigation of Two Low Alloy High Strength Steels", paper presented at the 18th Conference and Corrosion Show of the National Assoc. of Corrosion Engrs., Kansas City, Missouri, March 19-23, 1962.
- (74) Swets, D. E., and Frank, R. C., "Hydrogen from a Hydrocarbon Lubricant Absorbed by Ball Bearings", Trans. Met. Soc. AIME, 221, 1082-1083 (October, 1961).
- (75) Swets, D. E., Frank, R. C., and Fry, D. L., "Environmental Effects on Hydrogen Permeation Through Steel During Abrasion", Trans. Met. Soc. AIME, 212 (2), 219-220 (April, 1958).
- (76) Chilton, J. E., "Development of Electroplating Processes to Eliminate Hydrogen Embrittlement in High-Strength Steel", WADC TR 57-514 (November 4, 1957).
- (77) Brown, Jack T., and Baldwin, William M., Jr., "Hydrogen Embrittlement of Steels", Trans. Am. Inst. Mining and Met. Engrs., 200, 298-303 (1954); J. Metals, 6 (2), 298-303 (February, 1954).
- (78) Toh, Taiji, and Baldwin, William M., Jr., "Ductility of Steel with Varying Concentrations of Hydrogen", Stress Corrosion Cracking and Embrittlement, W. D. Robertson, editor, John Wiley and Sons, Inc., New York (1956), pp 176-186.
- (79) Chang, P. L., and Bennett, W. D. G., "Diffusion of Hydrogen in Iron and Iron Alloys at Elevated Temperatures", J. Iron and Steel Inst., 170, 205-213 (1952).
- (80) Steigerwald, E. A., Schaller, F. W., and Troiano, A. R., "Discontinuous Crack Growth in Hydrogenated Steel", Trans. Met. Soc. AIME, 215, 1048-1052 (December, 1959).
- (81) Klier, E. P., Muvdi, B. B., and Sachs, G., "Hydrogen Embrittlement in an Ultra-High-Strength 4340 Steel", J. Metals, 9 (1), 106-112 (January, 1957); Trans. Am. Inst. Mining, Met., and Petroleum Engrs., 209, 106-112 (1957).

- (96) Petch, N. J., "The Lowering of Fracture Stress Due to Surface Adsorption", *Phil. Mag.*, Series 8, 1, 331-337 (1956).
- (97) Morlet, J. G., Johnson, H. H., and Troiano, A. R., "A New Concept of Hydrogen Embrittlement in Steel", *J. Iron and Steel Inst.*, 189, 37-44 (May, 1958).
- (98) Steigerwald, E. A., Schaller, F. W., and Troiano, A. R., "Effect of Temperature on the Static Fatigue Characteristics of Hydrogen Embrittled 4340 Steel", WADC TR 58-178 (April, 1958).
- (99) Bilby, B. A., and Hewitt, J., "Hydrogen in Steel - The Stability of Micro-Cracks", *Acta Met.*, 10, 587-600 (June, 1962).
- (100) Garofalo, F., Chou, Y. T., and Ambegaokar, V., "Effect of Hydrogen on Stability of Microcracks in Iron and Steel", *Acta Met.*, 8, 504-512 (August, 1960).
- (101) De Kazinczy, F., "Crack Formation in Steel During Electrolytic Hydrogen Absorption", *TVF*, 32 (3), 159-165 (1961), In English.
- (102) Tetelman, A. S., and Robertson, W. D., "The Mechanism of Hydrogen Embrittlement Observed in Iron-Silicon Single Crystals", *Trans. Met. Soc. AIME*, 224 (4), 775-783 (August, 1962).
- (103) Siede, A., and Rostaker, W., "On the Problem of Hydrogen Embrittlement of Iron", *Trans. Met. Soc. AIME*, 212 (6), 852-855 (December, 1958).
- (104) Blanchard, P. A., and Troiano, A. R., "Hydrogen Embrittlement In Terms of Modern Theory of Fracture", WADC TR 59-444 (August, 1959).
- (105) Scott, T. E., and Troiano, A. R., "Interstitial Induced Delayed Failure of Steel", U. S. Air Force, Aeronautical Research Laboratories, ARL 62-425 (September, 1962).
- (106) Dauerman, L., "A Study of the Mechanism of the Action of Inhibitors Which Prevent Hydrogen Embrittlement of Carbon Steels Resulting from Acid Pickling", Rutgers University, Final Report for Paint and Chemical Research Laboratory, Aberdeen Proving Ground, on Contract No. DA-30-069-ORD-1680 (January 1, 1956, to November 30, 1960).
- (107) Beck, W., Klier, E. P., and Sachs, G., "Constant Strain Rate Bend Tests on Hydrogen-Embrittled High Strength Steels", *Trans. Am. Inst. Mining and Met. Engrs.*, 206, 1263-1268 (October, 1956).
- (108) Morgan, William A., "New Test for Hydrogen Embrittlement", *Digest of Reference 109, Metal Prog.*, 82 (1), 154, 156 (July, 1962).
- (109) Williams, F. S., Beck, W., and Jankowsky, E. J., "A Notched Ring Specimen for Hydrogen Embrittlement Studies", paper presented at 63rd Annual Meeting of the ASTM, Atlantic City, N. J. (June, 1960).

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