# Hydrogen in steel
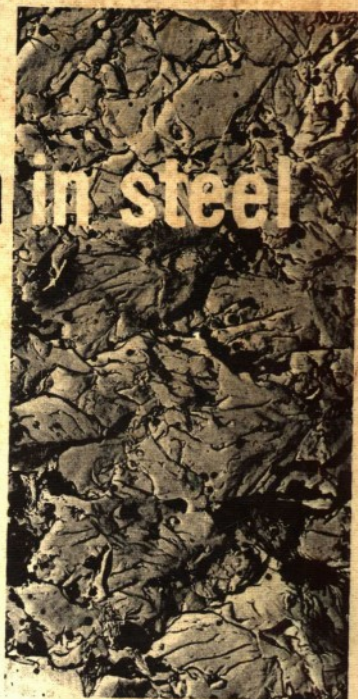
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# Hydrogen in steel

## Contents

# The influence of hydrogen
# on the mechanical behaviour of steel

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Relatively small amounts of hydrogen in steel can greatly influence its mechanical behaviour, particularly with respect to ductility related properties.

Brittle delayed failure with discontinuous crack propagation following a crack incubation period has been demonstrated for high strength steel. This has been related to the slow strain rate—temperature sensitivity characteristic of hydrogen embrittlement and also to strain-ageing embrittlement. Slow strain rate hydrogen embrittlement has been also observed in several face-centred cubic metals including austenitic stainless steel.

A new theory of hydrogen embrittlement is suggested which involves the concentrating of hydrogen in lattice solution near regions of piled-up dislocations associated with a high triaxial stress state. Crack incubation is brought about by diffusion of hydrogen and the consequent lowering of the fracture stress in such regions.

Mechanical behaviour, e.g. slow strain rate embrittlement, delayed failure, blistering of sheet, flaking, and stress-corrosion cracking, is briefly discussed in terms of the proposed mechanism.

It has long been appreciated that relatively small amounts of hydrogen in steel can greatly influence its behaviour. In general, after exposure to a hydrogen environment, either gaseous or chemically combined, steel will tend to lose ductility and may even develop cracks. In addition to embrittlement, other closely related phenomena associated with the influence of hydrogen environments encountered in processing or in service, include flaking or hair line cracking, blistering, spalling of electroplated finished, brittle delayed failure, discontinuous crack propagation and stress corrosion cracking.

The solubility of hydrogen in ferrite is virtually negligible at ambient temperatures and becomes barely measurable at $800^{\circ}F$. At the temperature of the alpha to gamma transformation, the solubility increases abruptly and continues to increase in linear fashion above this temperature to the melting point. At any temperature, equilibrium calls for the rate of formation of nascent and molecular hydrogen to be equal. It can easily be shown that the amount of hydrogen dissolved at a given temperature is proportional to the square root of the hydrogen gas pressure outside the steel. This is the well-known Sievert's law.

$$C = K \, (PH_2)^{1/2}$$

Because of the sharp decrease in solubility of hydrogen with lowering temperature, steel when cooled from saturation at elevated temperatures will be highly supersaturated. Greatly increased partial pressure of atomic hydrogen would be required to hold this excess hydrogen in solution in the crystal lattice—a situation not normally existent, in view of the extreme stability of hydrogen molecule at ordinary temperatures. Supersaturation can also be obtained as the result of chemical or electro-chemical action which may provide, in effect, an extremely high external pressure of atomic hydrogen. On removal of this source of hydrogen, supersaturation will exist just as in the case of cooling.

Hydrogen dissolved in the lattice by either of these methods will diffuse out of the metal lattice and recombine to molecular hydrogen. This can occur either in the atmosphere near the surface of the steel or within the steel in discontinuities or voids.

In this latter case, the pressure of molecular hydrogen will be built up in the voids according to the square root relationship until the equilibrium pressure is attained. It is possible to apply the mass action constant to Sievert's

solubility data and calculate pressures well in excess of the tensile strength (1). A critical aspect of the concept of very high pressure in voids involves the size of the voids. The voids must be large with respect to the size of a unit cell—sufficiently large for theory to apply. That is, the voids must have true surfaces and sufficient volume for the elements of kinetic theory to be applicable.

The above simple relations have been known and accepted for some time and have set the stage for the most widely held theories of hydrogen embrittlement. However, before we consider the various theories let us briefly examine some of the characteristics of the mechanical behaviour of hydrogenated steel. One of the most intriguing aspects of this embrittlement is its sensitivity to strain-rate and temperature. Briefly, the embrittlement is enhanced by slow strain-rates and moderately elevated temperatures. These are mutually dependant variables and may be perturbated over a wide range of strain-rate and temperature (2-7). The upper temperature limit is set by the temperature at which appreciable outgassing will occur. This is, of course, precisely the converse of the more conventional behaviour, where high strain-rates and low temperatures enhance brittle behaviour and give rise to the so-called transition behaviour of steel. This slow strain-rate and temperature sensitivity imparted by hydrogen strongly suggests that the phenomenon is under the control of and paced by the diffusion of hydrogen.

Other mechanical phenomena have been related to the influence of hydrogen. For example: it has been demonstrated that hydrogen does not change the flow stress or ultimate strength of steel but merely chops off the stress-strain curve at reduced values of strain and, of course, at correspondingly reduced fracture stress. Notch impact tests will not usually exhibit hydrogen embrittlement, but the finite fatigue life is definitely impaired by the introduction of hydrogen. Much of the mechanical behaviour outlined here has been determined and catalogued by members of this group, such as, Hobson, Sykes, Hewitt, Burton and others.

The theory of hydrogen embrittlement which has received the widest acceptance, at least until quite recently, is the planar pressure theory. In essence, it involves the precipitation of molecular hydrogen in voids with a concomitant build-up of high pressure as described earlier. These localized high pressures tend to compress the surrounding metal, developing a high degree of localized triaxial tensile stresses. This state inhibits extensive

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slip thus restricting plastic deformation and promotes brittle behaviour (8).

The theory has been reasonably successful in explaining much, but not all, of the mechanical behaviour. Blistering, for example,is easily explained in terms of the pressure build-up. The slow strain rate and temperature sensitivity find their rationalization in the time-temperature relations for the diffusion rate of hydrogen necessary to deliver hydrogen to the voids at a rate sufficient to maintain a critical embrittling value of pressure as the voids are opened during straining.

Some of the other mechanisms are, broadly speaking, variations of the planar pressure theory. For example, the refinement introduced by Bastien and Azou lies primarily in the mechanism by which the hydrogen is delivered to the voids (9). They suggest that hydrogen is concentrated around dislocations as a Cottrell atmosphere. Under strain, the dislocations travel through the lattice. Whenever these hydrogen-laden dislocations reach a void, some of the hydrogen is discharged into the void, thus increasing the pressure and causing embrittlement.

Another variation of the pressure theory has been presented by de Kazinczy (10). In his viewpoint, the contribution of the hydrogen gas in the void to the energy necessary for crack propagation arises from the expansion of the gas during crack growth. This mechanism is based on the principle that expansion of a gas is accompanied by a release of energy. Thus, expansion of the hydrogen gas during crack growth releases energy and thereby lowers the applied stress necessary for crack propagation. Continued crack growth depends upon continued increase in energy content of the gas in the crack. This is provided by hydrogen diffusion to the crack and precipitation therein. Thus, the embrittlement is diffusion controlled and would tend to disappear at high strain rates and low temperatures.

A quite different theory has recently been developed by Petch and co-workers (11). They suggest that fracture arises from the formation of a crack ahead of an array of dislocations piled up against a grain boundary. Because of adsorption of hydrogen on the surface of the crack as it forms, the stress required for fracture is lowered. The influence of strain rate and temperature is again quite readily explicable on the basis of the diffusion of hydrogen which will control the delivery of hydrogen to the crack edge.

Research at Case Institute of Technology has led us to postulate still a different mechanism of hydrogen embrittlement. This has come about largely as the result of the examination of several relatively unexplored mechanical phenomena directly associated with the presence of hydrogen—specifically, brittle delayed failure and discontinuous crack propagation (2, 12-15).

I should like to describe these studies and develop in some detail a model of hydrogen embrittlement and finally discuss other known hydrogen induced phenomena in steel in terms of this model.

All brittle failures involve the initiation and propagation of cracks. Under the conditions of relatively slow strain-rate controlled by diffusion of hydrogen, the times for crack initiation and propagation become highly significant and readily measurable over broad operating ranges of time and temperature. An analysis of this type of failure will, then, involve a measurement of the time for crack initiation or more specifically the crack incubation period, and a determination of the rate and mechanism of crack propagation to failure.

For an examination of this type, sustained load tests at different initial stress levels and test temperatures offer definite advantages in crack initiation and propagation studies as compared to tests where the load and the stress are continuously increasing, often at relatively high rates.

Uniformly hydrogenated notched tensile specimens were dead-weight loaded at different stresses and the failure

characteristics noted (12). The conditions of test temperature and strength level were such that there was no visible evidence of creep at any applied stress level up to the unhydrogenated notch tensile strength.

Figure 1 typifies the kind of sustained load to failure curves that were obtained.

There are a number of significant features that should be noted here:

1. The notch tensile strength may be less than normal and directly reflects the loss of ductility due to hydrogen

2. Delayed failure may occur over a wide range of applied stress.

3. There is only a slight dependence of the time to failure upon the applied stress.

4. Perhaps the most significant characteristic of this stress rupture relationship lies in the fact that there is a minimum critical value below which failure does not occur.

These are static fatigue curves, and the lower critical stress may be considered a static endurance limit. This behaviour is sensitive to hydrogen concentration as shown in the experimental curves of Figure 2. Most of the data to be presented have been obtained with a .40% carbon - Ni-Cr-Mo steel (AISI 4340).

It is significant to note that all delay failure parameters, notch strength, rupture time, and static fatigue limit increase with decreasing hydrogen concentration.

Also note that even after 24 hours at 300°F there is still a substantial stress range, of the order of 60,000 psi over which delayed failure will occur. In fact, the notch tensile strengths on the curves of Figure 2 indicate complete recovery after 7 hours at 300°F, yet delayed failure will still occur over a wide range of applied stresses. Thus, it is apparent why conventional laboratory tests may not detect the susceptibility to delayed failure.

The increase in lower critical stress with decreasing hydrogen concentration suggests that crack initiation is controlled by a combination of hydrogen and stress. With decreasing hydrogen concentration, more stress is necessary to initiate delayed failure. The concept is supported by experiments on specimens of varying notch severity (Figure 3). It is evident that the static fatigue limit rises as the notch severity decreases. The unit stress at the roof of the notch is high and undoubtedly sufficient to cause localized plastic flow.

Thus, it appears that a critical combination of stress state and hydrogen concentration must be attained to initiate a crack. Additional support for this hypothesis is obtained from an examination of the position of crack initiation as a function of the notch severity. Sharply notched specimens crack slightly below the notch bottom as indicated in Figure 4 and less sharp notches more deeply. These results agree qualitatively with the concept that the most severe triaxial stress state exists below the notch surface, and that the position of maximum triaxiality moves into the specimen as the notch severity is decreased. This fixes the location of crack initiation at the position of maximum triaxial stress. Let us now direct our attention to the events occuring prior to fracture in the static fatigue stress range. The kinetics of crack initiation and propagation can be followed by electrical resistance changes (16). Figure 5 shows a typical resistivity-time curve for sharply notched specimens. A true incubation period for crack initiation and a period of apparently controlled crack propagation are apparent.

The existence of an incubation period is a matter of considerable importance. It is self-evident that, for a given incubation period, a slow strain-rate test will be more likely to detect embrittlement than a high strain-rate test. If the strain-rate is so high that the specimen fractures in less time than the incubation period, then hydrogen embrittlement will not be detected. This behaviour must be reflected in the

design of a suitable test for detection of hydrogen em-
brittlement. Apparently, a mechanical test will be inade-
quate if the test duration is less than the incubation period.
Since we have observed incubation periods of substantial
duration, short time tests such as normal tensile and bend
tests may not be discriminating. Thus, under these con-
ditions, the steel may exhibit normal tensile ductility but
will still be subject to brittle delayed fracture (17).

The hydrogen induced incubation period for crack initia-
tion is interpreted in the following manner. Just prior to
testing, the hydrogen is uniformly distributed throughout
the specimen. The proper or critical concentration of
hydrogen for failure does not exist in the region of high
triaxiality because the specimen does not fail on loading;
but since the load or stress does not change, the incuba-
tion time must be that time necessary for the hydrogen to
concentrate in this region (12). It has been demonstrated
that the driving force for diffusion is an activity gradient
for the diffusing element. In this case the activity gradient
must arise from the non-uniform stress state, since the
hydrogen is uniformly distributed (18).

For stress-induced diffusion, the drift velocity of an
interstitial is directly proportional to the strain gradient
and the diffusion coefficient and inversely to the absolute
temperature.

$$V = \frac{D}{KT} F$$

In addition, the diffusion coefficient varies exponentially
with the absolute temperature.

$$D = A_e^{-Q/RT}$$

Thus, if the first initiation of a crack is dependent upon
the diffusion of hydrogen, then an Arhennius plot should
yield a linear relationship. The results shown in Figure 6
indicate that this is indeed the case and an activation
energy of 9200 cal. per mole is in good agreement with
several of the previously reported values for the diffusion
of hydrogen in alpha iron (19).

The failure process may be divided into 3 distinct
stages, as indicated by the resistivity curves:

1. The incubation period.

2. A period of relatively slow crack propagation.

3. Catastrophic failure with extremely rapid crack
   growth.

An interpretation of the incubation period has been pre-
sented. Let us turn our attention to the other two stages.
The appearance of the fracture allows one to differentiate
between these latter two stages, and thus to calculate the
fracture stress. This was a constant and approximately
equal to the value for the unembrittled material over a
wide range of hydrogen concentration and applied stress.
This simply means that the crack progresses slowly at a
rate controlled by hydrogen diffusion to a region near the
crack tip.

Thus, the implication is that crack propagation is a
discontinuous process and, in fact, consists of a series of
crack initiations. The most severe triaxial-stress state
will arise just slightly in advance of the crack. When the
critical hydrogen concentration is attained, a small crack
forms and grows through the hydrogen-enriched region,
thus joining the previous crack. Further crack growth
must await diffusion of hydrogen to the new region of high
stress state.

Resistivity curves taken at room temperature, (Figure 5)
are not revealing but  similar curves at lower tempera-
tures where the diffusion rate of hydrogen is retarded  yield
clear evidence in support of this hypothesis (see Figure 7).
It is apparent from the abrupt resistance increases that the
crack propagates in a discontinuous manner. After each
step of instantaneous growth a plateau of constant resis-
tance is present. The plateaus of constant resistance are
the "secondary" incubation periods. As the temperature is

lowered the plateaus become longer and the  individual
crack extensions become larger. Finally, at -50°F., the
first crack propagates instantaneously through the specimen
(19).

The hydrogen induced failure process is considered to be
essentially a normal fracture on which has been superim-
posed the embrittling influence of hydrogen. The external
specimen notch produces a local stress concentration. Plas-
tic flow occurs at the base of this notch and generates frac-
ture embryos in the form of blocked dislocation arrays.
These arrays which act as microcracks can be produced by
dislocation blocking at grain boundaries, by dislocation
coalescence on a non-slip plane, and by formation of a
shear stress field, such as occurs in the triaxial region
beneath a notch (20-24).

At a given value of applied stress, below the notch ten-
sile strength, a stable configuration of dislocation arrays
should exist. However, the stress concentration due to the
external specimen notch plus the microscopic concentration
of the array are not sufficient to produce localized fracture.
Hydrogen is attracted to the stress field of the array and
when the combination of stress and hydrogen concentration
in the lattice at the tip of the array is sufficient, localized
fracture occurs. The crack propagates until stopped, pro-
bably by passing out of the influence of the hydrogen rich
region and then the sequence of stress-induced diffusion
and localized fracture must be repeated, giving rise to the
discontinuous propagation.

Since the brittle failure is brought about by a series of
crack initiations, the factors involved in controlling the in-
cubation time should be highly significant parameters of the
mechanism. A basic component of the incubation time is the
relation between the hydrogen content and the stress neces-
sary to initiate a crack. It is possible to separate the role
of hydrogen content and stress and thus evaluate the contri-
bution of each. The crack incubation time is relatively in-
sensitive to the applied stress, strongly implying that the
process is dependent primarily on the development of a
critical hydrogen concentration.

At room temperature, as a result of stress-induced diffu-
sion during a mechanical test, the hydrogen content at the
point of crack initiation is not known. Thus, in determining
the stress-hydrogen relation to produce a crack, it is neces-
sary to test under conditions where the hydrogen concentra-
tion is not altered during the test. Such conditions are
attainable at low temperatures where the diffusion rate of
hydrogen is essentially nil.

Normal tensile tests were conducted at liquid nitrogen
temperature (-321°F) and the reduction in area served as
the parameter to measure embrittlement. The hydrogen
concentration was varied by regulating the charging current
density. The results are given in Figure 8 and clearly indi-
cate the relationship between hydrogen and stress necessary
to initiate a crack is primarily dependent on the hydrogen con-
tent. Below some critical quantity of hydrogen no embrittle-
ment occurs, but when this critical hydrogen is attained
catastrophic embrittlement takes place. The initiation of a
hydrogen-induced crack above some threshold stress is
therefore more dependent on the development of a critical
hydrogen content than on a critical relationship between both
hydrogen and stress.

The role of stress is primarily to produce the driving
force for the accumulation of the critical concentration of
hydrogen where the fracture embryo exists. There is, how-
ever, a minimum stress necessary to effect this critical
accumulation, less than this will develop some segregation
but not the critical amount (25). For dilute solutions, the
equilibrium distribution of solute atoms can be described in
terms of a Boltzman distribution function which has been
utilized to analyze solute segregation (26).

$$C = C_o e^{-U/KT}$$

where            $C$ = interstitial concentration at

any point,

$C_0$ = average interstitial content,

$U$ = interaction energy between the interstitial and the stress field,

$K$ = Boltzmann's constant, and

$T$ = absolute temperature.

The stress field about the dislocation array which serves as the fracture embryo may be expected to produce general effects on hydrogen which are governed by this equation. The concentration (C) of interstitial hydrogen about the array should be greatest where the interaction energy (U) is a maximum. This is at the region of maximum triaxiality where the fracture is first initiated. Thus, the analysis of the critical stress for failure can be restricted to this region.

On the basis of hydrostatic components, only the interaction energy can be expressed as

$$U = p \Delta v$$

where p, the average hydrostatic stress, =

$$- 1/3 \left( \sigma xx + \sigma yy + \sigma zz \right)$$

and $\Delta v$ is the change in volume produced in the lattice by the hydrogen.

The initiation of the crack is dependent on the development of a critical hydrogen content ($C_c$) at the lower critical stress or static fatigue limit. Here, $C = C_c$, and the distribution law applies

$$C_c = C_0 e^{-U_m/KT}$$

where $U_m$ represents the interaction energy corresponding to the position of maximum hydrostatic stress.

Notches exist in all metals, whether they be metallurgical or mechanical, and their influence on a dislocation array constitutes an important component of the theory of fracture. Since the influence of a notch on a dislocation array resides primarily in its ability to concentrate the macroscopic stresses acting on the embryo, its action on the failure parameters is quite predictable and, in the case of external machined notches, amenable to experimental analysis.

For a given initial hydrogen content ($C_0$) and test temperature (T), the maximum interaction energy ($U_m$) should be constant and independent of notch geometry at the lower critical stress. As the notch acuity increases the applied stress required to develop a given interaction should decrease.

Now since $\Delta v$ is constant and independent of notch geometry, then

$$\left( \sigma xx + \sigma yy + \sigma zz \right) = constant$$

The term $\left( \sigma xx + \sigma yy + \sigma zz \right)$ can be expressed as the product of the sum of the three principal stresses resulting from the external notch and a constant corresponding to the additional stress concentration due to the dislocation array. Thus, the sum of the three principal stresses resulting from the notch is a constant, but since this sum can be stated in terms of the applied stress $\sigma_A$ at the static fatigue limit and a notch stress concentration factor $K_f$,

then                     $\sigma_A K_f$ = constant

and                      $K_f = \dfrac{constant}{\sigma_A}$

Figure 9 shows a plot of experimentally determined values of the inverse lower critical stress as a function of

the stress concentration factor.[*]

Now since the relationship in linear and extrapolates through the origin as predicted by the simple derived equation, the assumptions become quite credible. That is, that the distribution law applies, that there is an interaction energy which at the critical stress for failure is constant and independent of notch geometry and that hence the notch functions merely enable the critical stress state to be attained at different applied stresses.

In determining the critical stress state, the yield strength is the limiting parameter since it effectively provides a "cut-off" for the maximum value of stress which can be attained. Plastic deformation at the root of a notch will lower the stress concentration factor. Thus, for a given applied load in the range of small plastic deformation, the stress concentration factor will be greater as the yield strength increases simply because there will be less plastic flow.

On the basis of the distribution law, the interaction energy associated with the critical quantity of hydrogen is constant and independent of strength level of the material. Thus, the sum of the principal stress ( $\sigma xx + \sigma yy + \sigma zz$) is constant and independent of strength level. However, this sum is dependent on both applied load and stress concentration factor, and thus can remain constant with increasing yield strength only if the applied load, i.e., the lower critical stress, decreases. This is, of course, exactly what has been observed. The lower critical stress decreases as the strength level of the material increases and explains why the high strength steels are more sensitive to hydrogen induced failure.

This, then, is the action of hydrogen in steel. Although outside the specific scope of this lecture, it is interesting to note that all these phenomena have been observed in titanium and its alloys displaying alpha, alpha plus beta, and beta structures. Other materials in which slow strain-rate hydrogen embrittlement has been observed include Vanadium, Columbium and indirect evidence indicates its presence in Molybdenum and possibly Tantalum. All of the metals considered thus far are body-centred-cubic with the exception of alpha titanium which is hexagonal close packed.

It has generally been accepted that face-centred cubic metals will not display slow-strain rate hydrogen embrittlement. We qualify our statement with the term "slow strain-rate" to exclude those cases of hydrogen embrittlement attributed to the formation of hydrides. However, recent studies in our laboratory have revealed this phenomenon in nickel and a series of face-centred cubic alloys of various analyses centred around Ni-Fe, Ni-Cr, Ni-Fe-Cr, Ni-Cu, and Cu-Zn. As an example of the type of behaviour observed, Figure 10 illustrates the influence of strain-rate on an iron-nickel alloy heavily charged with hydrogen (29). The strain rate sensitivity is quite apparent and the specimens failed by the formation of numerous surface cracks (see Figure 11) with reduced ductility as compared to the behaviour of non-hydrogenated ones under ordinary test conditions. As the strain-rate increased the degree of cracking decreased while the ductility increased. Also, at very low temperatures no surface cracking and no difference in ductility between hydrogenated and non-hydrogenated specimens was observed. These are, of course, all the characteristics of slow-strain-rate hydrogen embrittlement.

X-ray diffraction studies of these alloys revealed a hydrogen-rich surface phase of the same crystal structure (beta phase) as the base alloy with an interface rather than a two phase region between the two phases, indicating a solubility gap for hydrogen. This will account for the lack of deep

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[*] The particular types of notches were employed for which complete stress analyses are available in the literature (27, 28).

penetration of hydrogen in these types of alloys, including particularly the austenitic stainless steels, and also provides a logical explanation why brittle delayed failure is not normally observed in such alloys (30), except, of course, under conditions of continued exposure to a hydrogeneous environment. Under such conditions, the failures are classified as stress-corrosion cracking but undoubtedly involve the same basic elements of the mechanism presented here.

On the basis of these findings, it should be possible to observe delayed failure and discontinuous crack propagation under the proper experimental conditions peculiar to the face-centred cubic materials. Such conditions entail hydrogen charging in depth, but with reduced concentration to avoid masking the phenomenon by cracking on loading. It is also necessary that moderately elevated test temperatures be employed to obtain reasonable mobility of the hydrogen in the face-centred cubic structures as compared to the body-centred cubic ones. Investigations in progress which satisfy such conditions have indeed demonstrated this behaviour. The curve of Figure 12 reveals the nature of brittle delayed failure in K-monel, tested at 400°F. There is a definite incubation time with slow crack propagation but there are insufficient data yet to plot the values (32).

Slow strain rate embrittlement is not a new phenomenon. The earliest evidence (almost 40 years ago) involves the so-called blue-brittle behaviour of steel, which is merely a manitestation of spontaneous strain ageing embrittlement caused by carbon and nitrogen; that is, the straining and ageing occur during the test (31). For carbon and nitrogen in steel, this occurs at moderately elevated temperatures where there is sufficient atomic mobility. For hydrogen, this requirement of mobility is satisfied at room temperature and even at moderately low sub-zero temperatures. On this basis, hydrogen embrittlement and strain-ageing embrittlement are merely different facets of the same phenomenon. However, it is of little help to seek an explanation for hydrogen embrittlement in strain-ageing embrittlement, because no satisfactory explanation for this latter phenomenon exists.

The Cottrell mechanism of dislocation locking by condensed atmospheres of foreign atoms has provided a reasonably satisfying explanation of the yield point phenomenon in strain-ageing but does not explain embrittlement. There is nothing in the mechanism that will account for the ductility loss. Dislocation locking will only bring about a rise of the flow stress with an attendant increase in strength, but strength and ductility are not, per se, reciprocal properties short of values approaching the theoretical strength. In addition, it is difficult to visualize that a dislocation pile-up which initiates fracture by raising the flow-stress to the fracture value will give rise to discontinuous crack propagation as observed. More specifically, it is difficult to rationalize the cessation of crack propagation once started.

We should like to suggest that the fracture strength, or if you wish, the cohesive strength of the lattice is lowered by the segregation of interstitials in the lattice at the region near the tip of the dislocation array prior to the actual initiation of the crack. This is considered to be an uncondensed atmosphere and as such permits the array to be a more active fracture embryo and allows a greater average concentration of the interstitial over a larger volume. Some preliminary speculation on how this may come about has been presented elsewhere (29, 33).

In brief, we have presented a concept of hydrogen embrittlement which requires the segregation of hydrogen in the lattice by a process of stress induced diffusion. The hydrogen in the lattice lowers the true fracture strength of the material roughly in proportion to the quantity present—thus, when segregated by the stress state in front of a crack will give rise to its discontinuous propagation.

This theory will, of course, explain the slow strain-rate and temperature sensitivity as do most of the others on the basis of a hydrogen diffusion controlled mechanism. Naturally, it provides an explanation for brittle delayed failure and discontinuous crack propagation, since it was spawned by a study of these phenomena.

The blistering of sheet steel, spalling of enamelled or electroplated surfaces and similar behaviour present no problem. The theory does not in any way rule out the build up of hydrogen pressure in a void under the continued influence of a hydrogen potential. However, it does specifically and unequivocally rule out embrittlement by pressure. Failures of this type can quite readily be rationalized on the basis that

(A) the pressure will contribute to failure as would any applied stress,

(B) conditions which promote high hydrogen pressures of necessity promote high lattice hydrogen concentration and hence embrittlement.

The formation of flakes or hair line cracks in steel has quite definitely been associated with the presence of hydrogen. Here again, we feel that the hydrogen in solution embrittles the lattice, and when sufficient stress is applied brittle failure ensues. However, there are inherent circumstances quite peculiar to the problem of flaking.

One of these is the incubation period for the formation of flakes which may vary from minutes to days. The theory readily accounts for this behaviour as it does for the incubation time for crack formation, which likewise may vary over a wide range of time. Another set of specialized circumstances involves the transformation of austenite. As this transformation proceeds, on cooling for example, the remaining austenite becomes increasingly enriched in hydrogen and thus more susceptible to brittle failure when subjected to stress (34-35). The stress may originate from any one or combination of sources. The transformation stresses accompanying the formation of alpha from gamma (particularly at low temperatures) are most effective in promoting hairline cracks since the stress is associated with those volumes of the metal most rich in hydrogen— that is, the austenite which did not transform at the higher temperatures. Other possible sources of stress include thermal stresses arising from unequal cooling, simple applied stresses and in some cases stresses due to hydrogen pressure may contribute to flaking.

The type of stress or combination thereof will greatly influence the character and distribution of flakes. Transformation stresses will give rise to the typical small fine hairline cracks. On the other hand, thermal (macro) stresses will produce fissures with the appearance of quench cracks (large and quite open). In the broadest sense we consider both of these two extremes to be "flakes", since they have a common origin.

Finally, we should like to mention, only briefly, that hydrogen may play the dominant role in stress-corrosion cracking. We have demonstrated that some face-centred cubic metals and alloys, including particularly austenitic stainless steel, may exhibit hydrogen embrittlement, brittle delayed failure, etc., when heavily charged with hydrogen. The conditions for continued severe hydrogenation at the surface to form the brittle beta phase usually exist quite ideally under the circumstances which lead to stress corrosion cracking where the hydrogen source is in the external environment and not internal. Indeed, it is quite significant that several recent investigators report discontinuous crack propagation in the stress-corrosion failure of austenitic steel (36).

Much progress has been made in recent years in understanding the behaviour of hydrogen in steel. The nature, number, and quality of the papers to be presented at this conference eloquently attest to this. However, despite this progress, there still exists considerable mystery and even

controversy regarding many of the fundamental aspects of hydrogen behaviour. Even such simple questions as where and in what forms the hydrogen resides in the iron lattice can provoke sharp discussion. The stimulation, discussion and exchange of ideas afforded by conferences such as this will eventually lead the way to a complete solution of the hydrogen problem.

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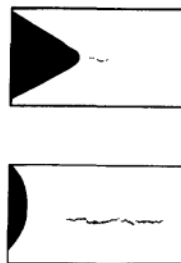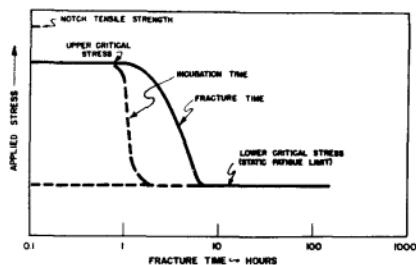
1 Schematic representation of failure characteristics of a hydrogenated high strength steel



4 Cracks observed in hydrogenated notch specimens sectioned after static loading. Longitudinal section at 100x. Top specimen has 0.001 in notch radius and bottom specimen has 0.010 in.
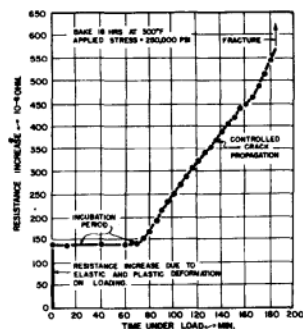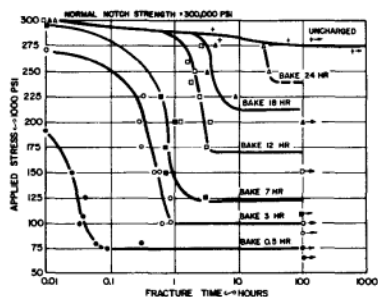


2 Static fatigue curves for various hydrogen concentrations obtained by baking different times at 300°F. Sharp-notch specimens. 230,000 lb/in² strength level.



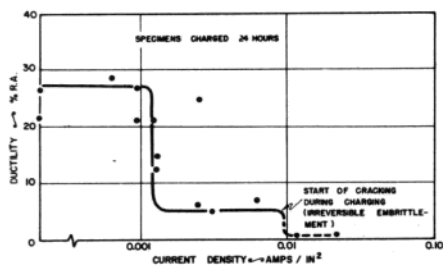5 Typical resistivity/time curve for sharp-notched specimens
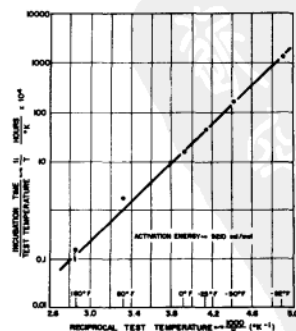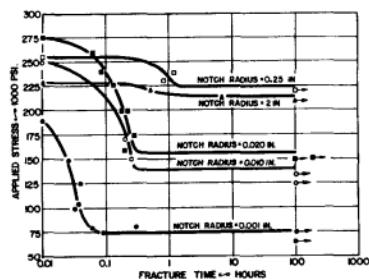


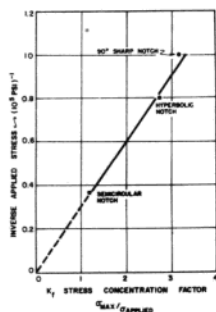3 Static fatigue curves for specimens of different notch sharpnesses. Baked 0.5 h at 300°F.



6 Ratio of incubation time to absolute temperature v. reciprocal absolute temperature. Applied stress 150,000 lb/in²
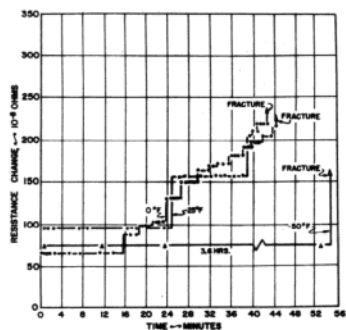
7 Resistance increase as a function of time for uniformly hydrogenated specimens tested in the stress range of delayed failure



10 Ductility at fracture as a function of strain rate in a hydrogen charged and uncharged 72%Ni-28%Fe alloy



8 Effect of hydrogen content (log current density) on the ductility of 4340 steel tested at -321°F



| CONDITION | UNCHARGED | CHARGED | UNCHARGED | CHARGED |
|---|---|---|---|---|
| TEST SPEED (IN/MIN) | 0.05 | 0.05 | 100 | 100 |
| %ΔR.A. | — | 36 | — | 0 |
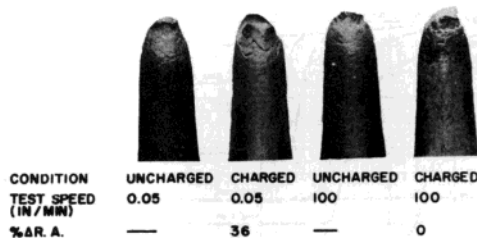
11 Fractured specimens of nickel tested at 23°C



9 Lower critical stress (static fatigue limit) as a function of the stress concentration factor calculated by relaxation methods. Hydrogenated 4340 steel
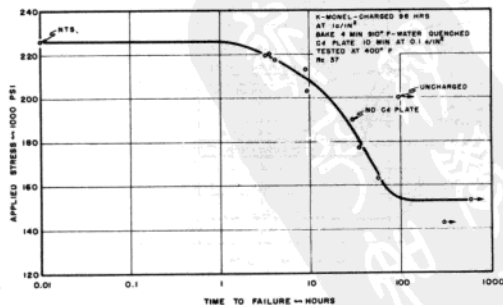


12 Static fatigue curve for hydrogenated K-monel. Sharp-notch specimens. 230,000 lb/in² notch tensile strength

# Discussion 1

The Chairman, Mr W.E. Bardgett, (The United Steel Companies Ltd) thought that the wide interest in the subject of hydrogen was evident from the breadth of representation at the conference with representatives from a number of research associations and educational establishments as well as from manufacturing firms and users, including Government establishments. They were not merely interested in manufacturing problems, but in the demands made on the steel and in the effects of its subsequent use.

What was the extent of past work on hydrogen? It has been dealt with by two sections of BISRA. The Gases and Non-Metallics Sub-Committee was instituted by BISRA Steelmaking Division in 1946 under the chairmanship of Mr. W. W. Stevenson to carry on the work of the Oxygen Sub-Committee, which had already made much progress in the analysis of hydrogen in liquid steel. The work was continued vigorously up to the publication of the first report of the Sub-Committee in December 1948. [1] The work on the sampling and analysis of hydrogen in liquid steel was regarded as almost complete, and reports on methods of hydrogen determination were subsequently published. Recently the need for work on the reproducibility of the results of hydrogen determinations had been suggested and this was to be considered.

The other activity was within the field of the Metallurgy Division. Before the formation of BISRA in 1946 there was a committee called the Hair-Line Crack Sub-Committee, under the chairmanship of Dr H.H. Burton, which published many interesting papers. After BISRA took over, further reports were published, but at a meeting of the Alloy Steels Research Committee held on 11 May 1949, 'it was agreed that the Hair-Line Crack Sub-Committee, having largely fulfilled its original function by substantially surveying the factors underlying hair-line crack formation, should be wound up'. The support given to academic research at universities was continued under the Alloy Steels Research Committee.

In the past there had been little co-ordinated activity in the field of hydrogen, at any rate in the UK, but a great deal of work had been carried out by individual investigators, and the idea of holding the present conference and obtaining an up-to-date assessment of the state of knowledge on the subject would be generally welcomed. The conference had been sponsored by the Alloy Steels Committee.

Dr J.D. Hobson (Hadfields Ltd) said that he had four questions to ask Professor Troiano. The first concerned the mechanism by which cadmium plating prevented the escape of hydrogen. In his own experiments in which high tensile steel was charged with hydrogen electrolytically, it had been shown that almost all the hydrogen was present in a very shallow surface layer. This technique of cadmium plating followed by baking to homogenize the hydrogen concentration depends upon impermeability and adhesion of the thin cadmium plate. Hydrogen diffusing at room temperature could generate high equilibrium pressures in cavities, sufficient to blister and crack the steel itself and to disrupt surface coatings such as enamel. It was therefore surprising that a thin film of cadmium had sufficient adhesion and impermeability to retain hydrogen. Could Professor Troiano explain the mechanism, and say whether thin deposits of other metals were equally efficient?

The second question concerned the amount of hydrogen required to produce delayed brittle fracture in high tensile steels. Electrolytic hydrogenation tends to produce erratic results, and it seemed unsatisfactory to assume that hydrogenated and cadmium plated specimens have a constant and homogeneous hydrogen content. Could Professor Troiano say what levels of hydrogen were present in the specimens being tested?

The third question was on steel composition. Most of Professor Troiano's results were obtained from tests on SAE-AISI 4340 steel, containing 0.4% C, 1½% Ni, 1% Cr and ¼% Mo. There was evidence suggesting that high tensile steel of the 5% Cr-Mo-V type was less severely affected by hydrogen than was SAE 4340. This might be due to an altered diffusion rate. Another variable arises from the two types being tested after significantly differing tempering processes, about 350-400°C for SAE 4340 and about 550°C for the 5% Cr steel. The two steels therefore differ appreciably in structure, and it would be interesting to have Professor Troiano's comments on this aspect of delayed brittle failure.

Finally, would Professor Troiano care to comment on the relationship between the mechanism proposed for hydrogen-induced delayed failure and that of hair-line cracking in large forgings and billets, which could still occur even though stresses induced by transformation and cooling have been reduced to a relatively low level?

Professor Troiano replied that the low solubility of hydrogen in cadmium was probably the major factor contributing to the impermeability of the cadmium plate. Corollary experiments involving time-temperature relations for recovery of hydrogen embrittlement yielded conclusive evidence that cadmium was a sufficient barrier to allow homogenization of hydrogen. They had had no experience with other metal films but evidence in the literature seemed to indicate that a chromium plate would be most effective in this respect. However, they felt that it would, in itself, have influence on the mechanical behaviour.

The question of the concentration of hydrogen required to produce brittle delayed failure in high tensile steel was most important and relevant. At the strength levels involved, the amount of hydrogen causing this catastrophic behaviour was extremely small. For example, they selected 3 heats from a large number of heats, 12-15 of the same type of steel, in which the as-received hydrogen content in the rolled bar stock was roughly 1 ppm in the first heat, 2 ppm in the second, and 3 ppm in the third. All three steels without hydrogenation behaved quite normally with no particular evidence of delay failure. Each one was hydrogenated in the same way and all displayed the same brittle delayed failure characteristics in a quantitative way. The hydrogen analysis of each showed the original content. They concluded that they had added to each steel an amount of hydrogen indeterminable by analysis. Because of the significance of this observation, no expense was spared to obtain the best hydrogen analyses available in several different places in the USA.

How should this be interpreted? The hydrogen was in two forms, at least. By the time the steel had been rolled and soaked, the hydrogen which was measured was largely in the voids and relatively unavailable for embrittlement (only hydrogen in solid solution can diffuse and cause

time-dependent brittle failure). How much hydrogen was added by hydrogenation? As to that, he relied entirely on what the analysts stated as the limit of detection, and the amount added must be something less than that; probably of the order of plus or minus 0.2 ppm.

They examined briefly another high tensile steel, an alloy with about 5% chromium with molybdenum and vanadium, probably not very different from that referred to by Dr Hobson. Experience did not indicate that the high-chromium steel was less susceptible than 4340. On the contrary, it appeared to be rather more susceptible. However, the high-chromium steel was more notch sensitive without hydrogenation than was 4340. The structure might well be different, strength level was significant in influencing susceptibility. The Professor could not say more without examining data for both steels under parallel conditions.

The conventional hairline cracks were essentially due to hydrogen embrittlement. The stress could originate from any one or combination of different sources, and for hairline cracks a major source would normally be transformation stress. He had never known a true 100% pearlite and ferrite structure to flake. However, such a situation would not be impossible if the hydrogen content were high and thermal or other stresses (not including transformation) were present. Quite often segregation in alloy steel would promote flakes. A good deal of work had been done in England on the analysis of these segregates, the origin of which has never been satisfactorily explained to him. These will not transform at the high temperatures and thus they give rise to the so-called 'hard spots' or 'raisins', providing transformation stress origins.

Mr P.I. Brittain (De Havilland Aircraft Co Ltd) said that in his company an attempt had been made, with some success, to measure diffusible hydrogen in steel by vacuum extraction, taking particular care to eliminate adsorbed water.

Figure A was a plot, ppm, of hydrogen diffusible at 300°C from stripped $\frac{1}{4}$ in. dia. specimens previously plated and baked for various times at 200°C. The results indicated that copper was readily diffusible to hydrogen, but cadmium was not, with zinc the worst. The figures obtained for cadmium seemed to correlate with sustained-load notched tensile results on 120 ton steel. Practically, it was important that they considered 100 or more as needed to reduce the hydrogen content by 50%.

Professor Troiano described Mr Brittain's remarks as most interesting, especially with respect to the action of zinc as a barrier to hydrogen.

Dr R.G. Baker (British Welding Research Association) discussed two points raised in the lecture. Professor Troiano said in his paper that although the Cottrell segregation explained the sharp yield-point in bcc materials it did not explain the loss of ductility during continuous straining. He had also said that embrittlement due to hydrogen was a problem analogous to that of loss of ductility due to carbon and nitrogen in the blue brittle range.

With regard to the first point, Cottrell had tried to relate the segregation of carbon and nitrogen to the explanation of the blue brittleness phenomenon which was a particular case of the Portevin-le Chatelier effect in steel.[2] It was possible to develop a theory by postulating that, at a certain temperature for a given strain rate, nitrogen atoms could catch up with dislocations. The dislocations then became locked and the strength increased. Before further deformation could occur, the stress had to be raised sufficiently to break the dislocations away from their atmospheres. During the subsequent breaking-away of the dislocations, the recorded stress fell and the whole process could then be repeated. This gave rise to the characteristically serrated stress-strain curve.

The work of Glen showed how interactions of this type could lead to loss in ductility. Glen had studied the effect of different alloying elements on the hot tensile[3] and creep[4] properties of various materials. He had shown that loss of ductility was encountered at different testing temperatures on the one hand, and at different amounts of total strain on the other, corresponding to the different alloying elements present. Thus, with regard to the first point, not only was there a theoretical model to explain loss of ductility during straining, but there was also supporting experimental evidence.

With respect to the second point, the effect of carbon and nitrogen in decreasing the ductility of steel in the blue brittle range could be explained in terms of their interaction with dislocations according to the theory proposed. The loss in ductility was accompanied by the Portevin-le Chatelier effect. In the case of hydrogen in steel at room temperature there was considerable embrittlement in straining, but there was no marked increase in strength, nor any evidence of the Portevin-le Chatelier effect. This suggested a marked contrast between the mechanism of embrittlement due to the carbon and nitrogen in the blue brittle range and to hydrogen at room temperature. He would appreciate any comments Professor Trioano might wish to make on this.

Professor Troiano replied that they might be discussing two different things. He had been dealing with loss of ductility rather than with yield phenomena. Concerning the first point, anything which required the locking of dislocations raised the strength, but there was never any evidence that hydrogen raised the strength of the steel. The work of Glen was most interesting and it was felt that it was closely related to discontinuous crack propagation they had observed in alloy steels 'dead-loaded' at temperatures near 800-1000°F. He was not ready to accept that the locking effects leading to higher strength were directly associated with the ductility loss. If his memory served him correctly Glen, and others, had noted that the increased strength and ductility loss were not coincident, as far as temperature was concerned.

The second point had to do with the embrittlement of iron at room temperature by straining and then ageing. He had not been aware that there was any serious embrittlement.

Dr Baker explained that he had been referring to the straining of a piece of iron containing hydrogen in solution.

Professor Troiano replied that there had been a misunderstanding. Although that experiment had not been reported in the lecture it had been tried. If one took iron (steel) which had been hydrogenated and then strained it one actually reduced the hydrogen embrittlement. If it were strained at a low temperature where one could introduce substantially more strain than at room temperature one reduced the hydrogen embrittlement was reduced. Deformation gave greater resistance to hydrogen embrittlement. Cold work opend up voids into which the hydrogen would go and thus become less available for embrittlement. Under certain circumstances it was possible to remove all evidence of embrittlement in this way.

Mr T. Boniszewski (British Welding Research Association) made some comments on cathodic charging of nickel with hydrogen. In some work at Cambridge with which he was associated they had charged nickel with hydrogen in 1N aqueous solution of sulphuric acid in the presence of cathodic poisons. They had found that, under certain conditions of charging, nickle hydride was formed at the surface of the specimens and the thickness of the layer of nickel hydride increased with charging time.[5] If nickel hydride was formed it led to the development of very heavy

grain-boundary cracks at room temperature after the specimen was held without any external stress being superimposed. If the charging was carried out at higher temperatures, e.g. about 80°C, nickel hydride was again formed, but it decomposed rapidly and cracking could be observed immediately after the charging.

He was referring to nickel hydride and not the beta phase, because in the layer of the hydride they and the other workers[6] had found that the ratio of hydrogen atoms to nickel atoms was constant and close to unity, about 0.7-0.8. Combining this with X-ray, electron diffraction, and microscopic examination, it was concluded that the new phase was an interstitial compound. Extreme care should be taken in using cathodic charging for study of hydrogen embrittlement in various metals. No one had yet proved the existence of hydrides in iron and steels, but, in nickel open to heavy charging, hydride could be formed. In such a case the embrittlement was no longer the so-called slow strain-rate hydrogen embrittlement.

If nickel testpieces after heavy charging were examined before they were submitted to the test, cracking might be found in specimens charged heavily at temperatures above room temperature, since hydride is then unstable and can decompose during the charging.

The first question which Mr Boniszewski wished to ask concerned the discontinuous propagation of the cracks. He referred in particular to the digaram of Fig.7 of his paper showing three tests carried out at various temperatures, one at 0°F, the second at -25°F, and the third at -50°F. At -50°F the curve had only one plateau, which was supposed to be the incubation period followed by instantaneous breakdown. This would mean that the propagation of the embryo crack must have occurred instantaneously right across the cross-section, because this first crack which apparently formed in the incubation period produced the fracture. On the basis of Professor Troiano's theory the strain-induced segregation of hydrogen necessary for crack propagation should have occurred simultaneously with crack incubation along the whole path travelled by the crack. Mr Boniszewski did not know whether this could have happened in specimens of the size that Professor Troiano used.

Secondly, there was the question of crack incubation as such. How did Professor Troiano know that the array of dislocations, i.e. an embryo crack, occurred not while the load was applied, but later during the 'incubation period'? If he admitted the existence of plastic deformation at the root of the notch, the crack could have occurred there on loading, but it would not propagate. During the so-called 'incubation period' hydrogen would segregate there, and when a sufficient amount had done so, the first step, which Professor Troiano called the incubation period, might be a first propagation step through the first grain. Then, this crack would meet the first grain boundary, would be arrested and would have to await a further supply of hydrogen.

Professor Troiano answered on the first point that in the case of the fracture at -50°F there was indeed only one incubation period and complete propagation of the crack to failure. It must be realised that the hydrogenation of the steel did not alter its normal behaviour with respect to embrittlement at low temperatures and high strain rates. They had done some supplementary experiments which seemed to confirm that at -50°F one was near the transition temperature for this sharply notched steel, and at -50°F it would fail in a catastrophic manner once a crack was initiated.

There was any amount of evidence for the statement that there was no cracking on loading. Incubation time varied with the different variables, and the subsequent incubations and steps were always completely different from the original incubation. The individual crack propagation steps were always very much deeper than could be accounted for by arrest at the first grain boundary.

Dr K. Sachs (GKN Group Research Laboratory) said that at high temperatures hydrogen was in solution in ferrite, but at room temperature most of the hydrogen was present in some other form, entrapped or adsorbed in lattice defects, grain boundaries, and incoherent interfaces. It had been widely held that hydrogen in interstitial solution in the lattice was harmless and that embrittlement was caused by hydrogen associated with defects. The propagation of a crack was then facilitated by the migration of hydrogen from the surrounding lattice into the crack and this explained the strain-rate dependence of embrittlement. Professor Troiano had demonstrated that, in delayed failure at least, the strain-rate dependence was due to accumulation of hydrogen ahead of the crack tip, i.e. migration over a much greater distance. How did hydrogen embrittle the material when it was present in the lattice in sufficient concentration? Professor Troiano's answer was that it lowered the brittle strength of the lattice, reversing the usual assumption that lattice hydrogen was harmless. If interstitial hydrogen lowered the brittle strength, the strain-rate dependence of embrittlement became a function of hydrogen concentration in the lattice, and Professor Troiano had some evidence to show that very high hydrogen contents can induce embrittlement at high strain rates.

But the concentration of interstitial hydrogen was much greater at high temperatures. If this was the dangerous form of hydrogen, one would expect brittle failure to occur most readily above about 200°C and to be independent of strain rate. This was obviously not the case.

One possible reason was that in this temperature range the cleavage strength, even when lowered by interstitial hydrogen, exceeded the yield strength. It should be possible to test Professor Troiano's thesis by raising the yield point and checking whether the introduction of hydrogen raised the transition temperature at high strain rates. Another explanation might be that at higher temperatures very high hydrogen concentrations were required to lower the cleavage strength. A test of Professor Troiano's theory would therefore require a study of the effect of hydrogen content on the temperature dependence of embrittlement. Hydrogen analyses were in any case essential for any demonstration that the normal strain-rate dependence of hydrogen embrittlement was due to the mechanism which Professor Troiano had established as the cause for delayed failure in ultra-high tensile steels.

Professor Troiano did not think that Dr Sach's contribution called for an answer. He agreed on the whole with what had been said. There was no question about the lower-strength steels requiring definitely measurable amounts of hydrogen to produce embrittlement effects. He therefore felt that if one put enough hydrogen into the steel to attain the critical concentration everywhere in the steel one should get slow strain-rate sensitivity. He would like to ask Mr Boniszewski what was the crystal structure of the hydride?

Mr Boniszewski replied that this was face-centred cubic, as with nickel, but that the lattice parameter was much greater; it was 3.721 ± 0.001 Å, which gave 5.6% lattice expansion.

Professor Troiano asked why Mr Boniszewski called that a hydride rather than a solid solution.

Mr Boniszewski replied that there was no definite indication that lattice expansion occurred continuously.

Professor Troiano said there was a solubility gap, similar to that of palladium. The solubility gap with the two-component system and the phase arch did not allow a two-phase field.

Mr Boniszewski, in reply, said that it was not exactly the same situation as with palladium.

Professor Troiano thought that they were observing the same phase.

Mr Boniszewski suggested that the mechanical implications were different.

Professor Troiano then referred to the slow strain rate failure which he showed for nickel. This made it very difficult to accept compounds.

Mr Boniszewski said finally that it depended on the thickness of the layer of nickel hydride.

Mr D.F.T. Roberts (United Power Company) referred to the considerable change in the diffusion constant of hydrogen at about 150°C and asked whether any evidence of this had been observed in the fracture at higher temperatures.

Professor Troiano replied that they had made no study of it at all. They had done some work at elevated temperatures but he had no grounds for making a definite statement.

Mr Roberts said that the importance of the yield strength had been emphasized. Could it be assumed that with very large quantities of hydrogen there would be interaction increasing the yield such as would occur at lower temperatures?

Professor Troiano was not sure that he understood the question . but said that the lower the yield strength the lower would be the maximum interaction energy which could be obtained. It was more than just the value of the yield; it was also the amount. They felt that flow reduced the stress state. and this reduction of the stress state would release the interaction energy. If the interaction energy was reduced to a point where it could no longer concentrate the critical amount of hydrogen, then the brittle delayed failure phenomenon would no longer be operative. It was necessary to study this phenomenon as a function of the strength level of the steel. They had done some of this work and at a yield strength level of about 130,000 lb/in$^2$ it was still observed.

There was a further variable. As the strength level was reduced creep occurred. at least at the higher stresses. The character of the static fatigue curve started to change, growing less sharp and bending over more, but they still had discontinuous crack propagation and an incubation period. The lower critical stress, as the amount of creep increased and the strength level went down, became less sharp; it was difficult to say just when the lower critical stress occurred. They were working on such problems at the time.

Mr P.R. Wedden (Westland Aircraft Company) asked whether he was right in assuming that the stage which Professor Troiano called irreversible embrittlement was denoted by the onset of hairline cracking. If so. was the static fatigue limit related to the magnitude of the current density necessary to produce irreversible embrittlement, i.e. would a material having a low static fatigue limit after cadmium-plating exhibit irreversible embrittlement at a low current density of cathodic charging?

Professor Troiano confirmed Mr Wedden's analysis of the irreversible embrittlement and its association with hairline cracking. He was not sure that a material with a low static fatigue limit would exhibit irreversible embrittlement at a low current density of cathodic charging. Presumably it would. if charging was sufficiently prolonged.

Dr G.F. Modlen (Brown-Firth Research Laboratories) said a change in hydrogen concentration was postulated around the specimen notch because of the macroscopic stress concentration. From a knowledge of the specimen dimen-sions and the diffusion rate of hydrogen, was it possible to get reasonable agreement with observed incubation periods?

Professor Troiano did not think it possible. He did not know whether the crack stopped the moment it left the region of high hydrogen. He would not expect it to do so; it had a certain momentum. and it had to slow down and then it stopped. The factor which slowed down and stopped the cracks could not be evaluated quantitatively, in his opinion.

Mr G. Jackson (Samuel Fox and Co Ltd) remarked that alloy steels made by the basic open hearth process contained up to 11 ml/100 g of hydrogen and it would appear that only very small amounts, i.e. ppm. were necessary to cause embrittlement. On vacuum degassing, the hydrogen level was down to less than 2 ml/100 g. which was parts per ten thousand, not ppm. Some people had said that hydrogen contents of 2 ml/100 g. though an arbitrary. figure, probably represented a safe level for large masses of steel in that they would probably be free from hairline cracks. Was this figure of 2 ml/100 g a realistic figure to take? Secondly, since the amount of hydrogen necessary to cause embrittlement was exceedingly small, was it possible to overcome the difficulty by any other method. since it would be difficult to reduce the hydrogen content of steel to the low levels required?

Professor Troiano. taking the second question first. pointed out that the hydrogen concentration required was very small at high stress levels. but as the strength level was reduced the tolerance for hydrogen increased. He was. however. somewhat confused by the hydrogen concentrations. He did not feel that they were as different as they appeared. As to a remedy. he did not know of anything. except the possibility of putting the hydrogen into some other form. Deformation helped. They had found that 12% deformation. under their experimental conditions. stopped hydrogen embrittlement. and lesser percentages caused a reduction. He was often asked if composition made a difference. There was nothing in their experience to indicate that composition made much difference. He had been asked if structure made a difference; they had tried two structures in which they could obtain high-strength. bainite and martensite. and that had made no difference. Some steels had more inherent resistance to notches than others, and if they compared one of those against the more notch sensitive type it seemed to be a little better. but it simply had a small advantage. and the two soon lined up.

Mr G.W. Weeks (De Havilland Aircraft Co Ltd). referring to the hydrogen contents which had been mentioned, asked whether it would be reasonable to suggest that. though the figures seemed to be accurate. they might not represent the true picture. Was not the hydrogen concentration likely to be much higher than was indicated by the analysis figure, the hydrogen being at the surface of the specimen?

Professor Troiano replied that if there was not a uniform hydrogen concentration that would be true; the average concentration might not have much to do with the initiation of the crack if there was not a uniform hydrogen content. They felt, however, that in the data they had obtained and that he had presented they had a uniform concentration.

Mr E.C. Pigott (South Durham Steel and Iron Co Ltd) put four brief questions. First, had Professor Troiano found any confirmation of the claims made in recent Russian literature that, as the hydrogen content increased, the ultimate tensile stress diminished? It had been claimed, for example, that a hydrogen content of 6 ml/100 g typically reduced the UTS of 1.5% Cr steel from 68.6 to 61.2 tons/in$^2$. It was known that such contents reduced the notched tensile strength.

Professor Troiano said that the answer was No, but they had not made a systematic attempt to evaluate this. They were quite satisfied from what they had seen in the literature that it did not; unless, possibly, the ductility was so reduced that this stress/strain curve was cut off short of maximum load.

Mr Pigott then asked if, since the voids being considered were very large in relation to the diameter of the hydrogen atom and molecule, it was justifiable to think of what was occurring in terms of gas kinetics? Should they not rather think of the whole thing in terms of fluid mechanics? If so, they could consider continuous flow into the region of the crack tip, rather than mere particle effusion.

Professor Troiano replied that he had been careful about this. Voids must be regarded as holes of substantial size. There had to be a real wall and there had to be true surfaces. He agreed with what had been said.

Mr Pigott, in putting his third question, said that Professor Troiano had referred to the relatively slow rates of propagation. Was it not true that the fairly fast rates of progression were a more or less consistent feature?

Professor Troiano replied that he had perhaps spoken in too simple terms. The actual movement was quite fast, but it was discontinuous. He should have said 'the apparent slow rate'.

Mr Pigott asked finally how Professor Troiano disposed of the apparent element of coincidence in the discontinuous fracture he had described. How did he explain the initiation of fracture at the different points almost simultaneously?

Professor Troiano, in reply, said that at the higher temperature, room temperature and above, there was no evidence that the crack was initiated at different points simultaneously. Indeed, the crack initiations were random and numerous, giving rise to the apparent smooth crack propagation curves obtained at room temperature. However, at the lower temperatures, one initiation anywhere on the circumference provided a fairly substantial crack propagation and there could be a fair number of these before failure or there could be as few as only one. They did not feel that there was a perfectly uniform initiation and radial progress of the crack; but exceptional precautions were taken to approach perfect uniaxial loading. If near perfect uniaxial loading was not achieved, then the data were not reproducible.

Mr J. Hewitt (Steel, Peech and Tozer), on the subject of hairline cracking, said that they had carried out tests on a billet sectioned at intervals and had found evidence that hairline cracks were discontinuous in growth. The growth continued over about a week, and if the number of cracks was plotted against time, the curve rose steadily with time; but then surprisingly the curve turned over and showed a decrease in the number of cracks with further time. The total length of the cracks, however, grew steadily, so that what they had observed was initially many small cracks and the growth of these into large connecting cracks. The difficulty then arose that, if one looked at the distance between the cracks and calculated how long it would take for hydrogen to diffuse and precipitate over this distance, the time involved was too long for the normal diffusion rates obtained by extrapolating high-temperature data. These data predicted times of the order of a few minutes or at most two or three hours. The actual process took a week. In all cases the incubation time bore no relation to this theoretical precipitation of hydrogen, and yet it seemed to be a precipitation phenomenon. Discrepancies of this type had led to more fundamental work on hydrogen in steel,

which had shown that only a small percentage of hydrogen in steel at room temperature is in insterstitial solution (0.1-2%), the residue being in some form of trap. The anomalous diffusion rates obtained by experiment at or about room temperature were, they believed, the rate of escape of hydrogen from these traps. These anomalous diffusion rates gave cracking times in good agreement with experiment. The propagation of these cracks was certainly controlled by migration of hydrogen to the crack.

In the examination of the theory of cracking and hydrogen embrittlement it seemed that the pressure theory, when modified, accounted very well for what was happening, but Professor Troiano's experiments and theory appeared to discount this pressure at the edge of the crack, and to favour the effect of hydrogen on the surface energy of the crack.

Considering the surface energy theory, the energy drop due to hydrogen was quite small, only a fraction of a percent of the total energy required to form the crack. Perhaps Professor Troiano would care to comment on these observations?

Professor Troiano agreed with many of the things that Mr Hewitt had said. Very little of the hydrogen was in the lattice and most of it was in the voids. The hydrogen pressure theory in its elementary form stated that high pressures were built up, which could be calculated. It was an enclosed volume with surrounding metal, and with hydrostatic compression, and there was therefore triaxial stress. The stress was raised, and presumably instead of plastic flow, brittle failure took place.

There were a number of objections to this: the simplest was that the hydrogen did not raise the strength. However, he did not rule out the possibility of hydrogen void pressure as a source of stress contributing to the crack extension of a hydrogen-embrittled material. Many of the other theories were simply modifications which depended on pressure for embrittlement: they had to be ruled out in the same way. In several theories the surface energy of the crack was lowered by the absorption of hydrogen. There were two objections to this. Even with brittle fracture there was some plastic flow, and the small amount of plastic flow involved relatively huge energies compared to the energy change from an absorbed surface to a clean surface or vice versa. Rough calculations made by X-ray measurement, presumably of the surface of what had been a brittle fracture by X-ray diffraction, and an attempt to convert this into energy showed that the figures came out several orders of magnitude as large.

The second difficulty was that he did not understand how either method of absorption would stop a crack once it had started. If he had to choose between the two he would choose absorption, but he did not feel that either was right. It was necessary to have an entirely new approach; they were trying to postulate the true fracture strength of the material. The bonds between the atoms were reduced by the hydrogen. He was aware of the weakness of this theory. The interaction energies involved seemed to be too small; but one did not really know. It was possible to calculate roughly the interaction energies, which were of the order of 0.1 to 0.2 eV. It was possible indirectly to ascertain the critical amount of hydrogen involved. It involved a long extrapolation, but there were curves showing the hydrogen concentration as a function of the charging current density. The amount came out at something like 8 ppm of hydrogen, and that seemed to be a very small amount of hydrogen to have this effect.

Mr Hewitt added the comment that the hydrogen atom in steel is usually an isolated particle. For example at normal hydrogen levels there would only be one hydrogen atom to every 4000 iron atoms; this did not appear to be sufficient to account for the macroscopic failures one observed in practice.

## WRITTEN CONTRIBUTIONS

Mr P.D. Blake (Murex Welding Processes Ltd) wrote: although the charging conditions in Professor Troiano's work are very carefully controlled, so that no blistering is obtained and embrittlement is reversible, there is a suspicion that all electrolytic charging of steel with atomic hydrogen may lead to some degree of plastic working, even below the surface, owing to the enormous hydrogen pressures developed. Whether this does in fact occur and whether this modifies the course of embrittlement as compared to charging a metal with molecular hydrogen either under pressure at 650°, at 1 atm pressure at about 1000°C, or in the liquid state, does seem to me to remain an open question.

Professor Troiano states that the amount of hydrogen involved in delayed failure of high tensile steels is below the limits of analysis. This presumably means less than about 0.1ppm. However, it is necessary to make the comment that, unless the effect can be definitely established by analysis as being due to hydrogen, there remains the possibility that the various baking times to which the steel is submitted to vary its hydrogen concentration may be causing some other change which is as yet unknown. I am prepared however to accept that hydrogen is the most likely element involved in the delayed failure.

Professor Troiano replied to Mr Blake that heavy electrolytic charging would give X-ray diffraction line broadening which did not disappear on baking, thus indicating plastic flow. However, with less severe charging conditions complete recovery of the X-ray diffraction effect was possible on removal of the hydrogen by baking, indicating no permanent plastic strain under these conditions.

Mr F. Watkinson (British Welding Research Association) wrote: with reference to Professor Troiano's lecture I would like to draw attention to certain differences between his results in dead-load rupture testing and ours.

Our results fail to show any delay in fracture occurring at high stress levels. If such conditions exist, then, using our testing procedure, the fracture delay time must be less than 0.3 min. This is illustrated in Fig.B.

The specimens used in our tests were thermally charged with hydrogen by soaking them in an atmosphere of hydrogen at a temperature of 950°C for half an hour and then quenching with an argon blast. This method gave reproducible hydrogen contents of the order of 4 ml/100 g, the exact value being dependent on the composition of the steel used, and it also produced as-quenched microstructures. The latter is considered to be the main factor contributing to the difference in behaviour even though the hydrogen contents may be higher than those of Professor Troiano's specimens.

The possible significance of Professor Troiano's results and our own, with respect to weld heat-affected zone cracking and the effect of post-weld heating, is apparent. Welding produces as-quenched microstructures which are incapable of supporting relatively low stresses. Post-weld heating may have the double effect of allowing rapid diffusion of hydrogen away from the weld zone and of tempering the microstructure to a form capable of sustaining higher stresses for longer periods.

Professor Troiano replied that he would be inclined to believe that several other factors might contribute to the difference in behaviour to an even greater extent. These would include the different manner in which the hydrogen was introduced and, in the absence of more specific information, the presumed difference in the test specimen geometry. He agreed with Mr Watkinson on the influence of post-weld heating.

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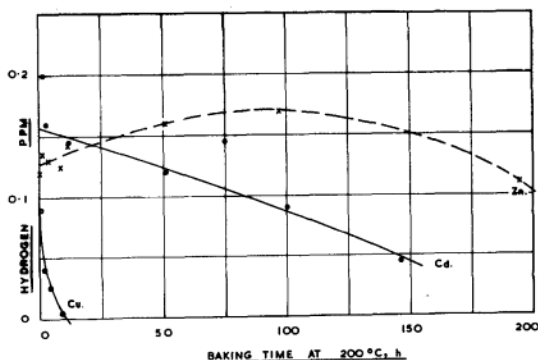
A    Effect of baking plated DTD 551 at 200°C
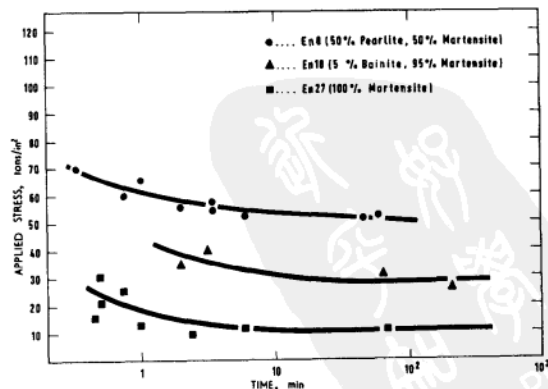
B Relation between fracture delay time and applied stress in dead load rupture tests on three steels