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(Metallurgy)
THE ABSORPTION OF HYDROGEN BY
HIGH TENSILE STEELS DURING CATHODIC POLARIZATION
IN AQUEOUS SOLUTIONS.

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degree of
Doctor of Philosophy

by

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A study has been made of the hydrogen absorbed by a high-strength steel during cathodic polarization in near-neutral solutions using rigidly controlled experimental conditions. Direct hydrogen analysis by the vacuum heating technique has been utilized and it has been established that use of high extraction temperatures (i.e. > 300°C) can lead to errors which are probably associated with a reaction between adsorbed water and the steel. Extraction at 200°C has been found to give satisfactory results free from this error.

The linear relationship between hydrogen absorption and time observed during the early stages of polarization in solutions above pH 4.0 was considered to be characteristic of a rate-controlled slow discharge mechanism of hydrogen evolution. The relationship between hydrogen absorption and overvoltage has been studied in the range pH 4 - 10; the results were found to conform with those anticipated from the kinetics of hydrogen evolution. Metallurgical structure was found to exert a strong influence on the ability of the steel to absorb hydrogen, and a modification of previous theories on delayed failure due to hydrogen has been proposed on the basis of the present study. The influence of arsenic additions to the solution on hydrogen absorption during cathodic polarization have been studied. It has been found that there is a region of pH and
overvoltage where hydrogen uptake is inhibited and these results have been correlated with sustained load experiments.

The results of this study have been utilized in an attempt to establish whether delayed failure may result from galvanic action produced by discontinuous coatings of electronegative metals (Cd and Zn) on high-tensile steels.
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SECTION 1. INTRODUCTION

The use of high-strength steels (i.e. having an ultimate tensile strength of 100 tons/in² or more) is becoming of widespread interest in the field of aircraft manufacture. Such interest is stimulated not only by the high strength/weight ratio of these steels, but also by their high strength/volume ratio. Since they contain only small amounts of alloying elements their resistance to corrosion, although slightly greater than that of mild steel, is not nearly so great as that of the highly-alloyed stainless steels. Thus it is necessary to apply protective metallic coatings to prevent them from rusting. The coating metals usually used are aluminium or cadmium, both of which are anodic to steel in service and therefore confer sacrificial protection on the steel at pores and discontinuities in the coating.

Application of these coatings usually involves either spraying or electrodeposition preceded by cleaning and at some stage in the overall process immersion of the steel in an aqueous solution is often necessary. It is well known that exposure of iron and iron/carbon alloys to aqueous solutions can result in discharge of hydrogen ions at the metal/solution interface and subsequent absorption of hydrogen by the metal. Furthermore, since hydrogen is known to be a contributory factor to embrittlement of iron and steel at room temperature, it is evident that aqueous treatments of these alloys presents serious problems.
In addition to the risk of developing embrittlement during cleaning or electrodeposition processes it is possible that the use of metals such as cadmium and aluminium as protective coatings may result in hydrogen absorption during service. Reference has already been made to the fact that these metals under service conditions are electronegative to the steel substrate. Although this is advantageous in the respect that the steel is protected at pores and discontinuities in the coating by sacrificial action, cathodic polarization of the steel at these areas may result in reduction of the hydrated proton (H$_3$O$^+$) with consequent entry of hydrogen into the steel.

Before proceeding further with a more detailed consideration of this problem, it is first necessary to review the literature concerning hydrogen absorption and embrittlement of iron and steel in general.
SECTION 2. LITERATURE REVIEW

2.1 Introduction

It has long been recognised\(^1,2\) that absorption of hydrogen by iron and steel can result in embrittlement of the metal at room temperature. When the source of hydrogen is a chemical or electrochemical reaction between the metal and an aqueous solution embrittlement is usually indicated by partial or complete loss of ductility in, for instance, a tensile test.\(^3\) It should be emphasized, however, that hydrogen embrittlement is not confined to iron and steel, but has also been reported for titanium,\(^4\) zirconium,\(^5\) uranium,\(^6\) vanadium,\(^7\) tantalum,\(^8\) molybdenum\(^9\) and tungsten.\(^9\)

With high-strength steels (i.e. having a U.T.S. of 100 tons/in\(^2\) or more) the presence of hydrogen in the metal can be particularly dangerous because of its ability to cause premature brittle fracture under sustained (static) tensile loads appreciably less than the U.T.S. of the material. This phenomenon is known generally as delayed failure\(^10\) or alternatively as static fatigue.\(^11\)

An extensive literature survey dealing with all aspects of hydrogen embrittlement of iron and steel was published by Buzzard and Cleaves in 1951.\(^12\) A review of hydrogen embrittlement of metals in general was published by Cotterill in 1961.\(^13\)

Hydrogen in iron and steel may arise from one of several sources, the most important of these being:

(1) Hydrogen dissolved in molten steel during manufacturing (or welding) processes and subsequently retained in the lattice of the metal after solidification,
(2) hydrogen absorbed during exposure of solid iron or steel to a hydrogen-containing atmosphere at elevated temperature,

(3) hydrogen absorbed during chemical or electrochemical reactions which take place at the metal/solution interface on immersion of the metal in an aqueous solution or during a corrosion process under service conditions.

2.2 The Fe/H system

Constitutional studies of the system Fe/H began about 1862 when large quantities of hydrogen were collected from electrolytic iron by Meisinger. In 1907 Sieverts and his colleagues commenced their classical studies of absorption of hydrogen by iron from the gaseous phase at elevated temperature. As a result of this work two important facts were established. Firstly it was shown that the gas dissolved atomically and secondly the composition of the Fe/H alloy was found to vary as the square root of the hydrogen pressure:

$$H_{metal} = K (P_{H_2})^{1/2}$$

This relationship has since been known as Sieverts' Law.

Since Fe/H alloys are pressure-sensitive the system can only be properly depicted in three dimensions and a satisfactory model has yet to be proposed.

An endothermic hydride has often been assumed to be responsible for hydrogen embrittlement of iron and steel but the
existence of such a compound has never been definitely established. Furthermore, since embrittlement has been found to occur at extremely low atomic ratios of H/Fe (e.g. 1 in 100,000) it appears unlikely that a hydrogen-containing compound is responsible.

X-ray studies have shown, with two exceptions, that hydrogen does not have any effect on the lattice constant of iron. Smith [20] has suggested that in these exceptional cases the metal was charged from arsenical electrolyte solutions, and the small displacements noted in the X-ray patterns could have been due to combination between iron and arsenic.

2.3 Manifestations of Embrittlement

Detection and evaluation of the possibility of hydrogen embrittlement resulting from a given operation must necessarily be based on some mechanical property of the material which is significantly affected by hydrogen. It was mentioned previously that the ductility of iron and steel is lowered markedly in the presence of hydrogen. [3, 21-24] Hence many workers have utilized tests based on this property in order to study hydrogen embrittlement. Determination of the decrease in % reduction in area and % elongation measured in a normal tensile test has been frequently carried out; [22, 25-28] slow bend tests [29, 30] in which either the required angle or the required number of reverse bends to failure are lowered when hydrogen is present have also been used. Smialowski [31] adopted a
torsion method suitable for the testing of wire which was reasonably sensitive to hydrogen.

High strength steels containing hydrogen exhibit the additional characteristic of susceptibility to delayed failure and thus evaluation methods based on this property have been widely utilized.\(^{31-34}\) In this form of test, axial loading of a plain (or notched) cylindrical specimen is usually carried out at a constant load below the U.T.S. of the material, and the time taken for the specimen to fracture noted. Although untempered, or very lightly tempered, high strength steels can fail in this way when hydrogen is totally (or very nearly) absent\(^{35}\) there is no doubt that the time taken to failure during such a test is reduced when hydrogen is present in the metal. Stressing is usually performed either by a weight and lever system, or by a spring system, stresses in the latter test being measured either by calibration of the spring or by direct observation of strain gauges attached to the specimen or its supports. In common with certain other forms of mechanical test (in particular fatigue testing) there is considerable scatter in the results. Statistical treatment of a large number of test results is often necessary thus making the method tedious and expensive (especially where notched specimens are concerned). With regard to sensitivity, however, the sustained-load method is probably superior to other mechanical tests for evaluating susceptibility of high strength steels to hydrogen embrittlement.
It is generally recognised that embrittlement due to hydrogen is not detectable by mechanical tests which involve straining at very fast rates \(^{27,28,36-39}\) (e.g. impact tests). This was conclusively shown in 1954 by Brown and Baldwin,\(^{40}\) who established that hydrogen decreases the ductility of steel only within certain ranges of test temperature and strain rate. They showed that the brittle range occurred in two domains, one at low temperature in which ductility rose with increasing strain rate but fell with increasing test temperature, and the other at higher temperature where ductility rose with increase in both strain rate and test temperature.

2.4 Investigations involving hydrogen analysis

Data concerning the relationship between the amount of hydrogen present (as measured by direct analysis) and the degree of embrittlement (as measured by mechanical tests) is very meagre. Indeed it is surprising that the first real attempt to correlate quantitatively the hydrogen content of steel with loss of ductility was not made until 1950, when Seabrook, Grant and Carney\(^{27}\) utilized the vacuum fusion method of analysis in conjunction with true-stress/true-strain tensile tests on cathodically charged SAE.1020 low alloy high strength steel. They showed that ductility was reduced progressively with increasing hydrogen content until a limiting minimum value in ductility was reached at a concentration of approxi-
mately 4.5 p.p.m. hydrogen; above this concentration no further reduction in ductility was found to occur. Hobson and Sykes\textsuperscript{26} carried out a similar investigation utilising the vacuum heating method of analysis in conjunction with true-stress/true-strain tensile tests on a 3\% Cr/Mo steel which was hydrogenated by heating in the gas at elevated pressure. They reported that hydrogen had little effect on the stress/strain curve until the 'apparent' maximum stress had been exceeded and 'necking' was in progress. Later Hobson and Hewitt\textsuperscript{28} also showed that for several steels (none in the very high tensile strength range) ductility was reduced with increasing hydrogen content, but no minimum in ductility was reported. They also suggested that for these lower strength steels, the critical level of hydrogen above which loss of ductility at room temperature commenced was between 1 - 1.8 p.p.m.

It would be extremely interesting to know whether the critical level for very high strength steels is lower than this value, since there have been conflicting statements on this subject; for instance Troiano et al\textsuperscript{41} were unable to detect any difference between hydrogen contents of high strength steels measured before and after hydrogenation, even in cases where ductility was shown to be drastically reduced. Troiano, however, does not state what method of analysis he used for determining hydrogen.

Methods available for hydrogen determination are reviewed in a later section.
2.5 Hydrogen absorbed during chemical or electrochemical reactions

Some of the earliest observations\textsuperscript{42,43} on hydrogen absorption and embrittlement of iron were made with hydrogen resulting from chemical or electrochemical reactions such as those occurring during pickling, cathodic cleaning or electrodeposition. The term 'absorption' is generally used to describe a process which essentially consists of three steps. These are as follows:

(a) adsorption of hydrogen on the surface;
(b) solution of hydrogen in the metal;
(c) diffusion of hydrogen into the interior of the metal.

Reduction of hydrogen ions at the metal/solution interface is a necessary pre-requisite to hydrogen absorption by the metal, and is usually considered to be an intermediate step in the overall hydrogen evolution reaction; these intermediate steps can be conveniently summarized as follows:

\[
\begin{align*}
\text{diffusion} & \quad \text{discharge} & \quad \text{combination} \\
\text{migration} & \quad \text{dehydration} & \quad \text{H}_2 \\
\text{convection} & \quad \text{M-H} & \quad \text{M-H} \\
\text{(H}_3\text{O)}^+ & \quad \text{H}_2 & \quad \text{M-H} \\
\text{sol.} & \quad \text{(H}_3\text{O)}^+ & \quad \text{M-H} \\
\text{elec.} & \quad \text{M-H} & \quad \text{or electrochemical} \\
\text{(a)} & \quad \text{(b)} & \quad \text{(c)} \\
\text{(a)} & \quad \text{(b)} & \quad \text{(d)}
\end{align*}
\]

Any one (or more) of these various steps may determine the overall rate of hydrogen evolution depending on the particular system, and when considering hydrogen entry into metals the mechani-
ism of the hydrogen evolution reaction must be taken into account. It has recently been suggested by Barton\textsuperscript{44} that entry of hydrogen into metals should be regarded as a side-reaction to the evolution reaction.

The relationship between the hydrogen evolution reaction and entry of hydrogen into iron and steel is discussed more fully in a later section.

(a) Adsorption of hydrogen on iron

Two individual types of adsorption can be distinguished, namely, physical adsorption and chemisorption (or activated adsorption).

Physical adsorption of hydrogen on iron usually occurs only at low temperatures and usually decreases as the temperature increases, being replaced at higher temperatures by chemisorption. Experimental results show that there is a definite relationship between the amount of hydrogen physically adsorbed by a unit surface area of a metal and the pressure at any given temperature,\textsuperscript{45} and that the process is reversible with respect to temperature and pressure.\textsuperscript{46} In the case of true or chemical adsorption the adsorbed layer will not be more than 1 molecule thick since the range of surface forces responsible for adsorption is usually less than the diameter of most gas molecules.\textsuperscript{47} With diatomic gases (e.g. hydrogen) Langmuir\textsuperscript{47} has suggested that there is evidence that the forces responsible
for adsorption act on the individual atoms of the gas rather than the gas molecules themselves.

Activated adsorption, or chemisorption, is a much more complex process and although chemisorbed hydrogen dissociates on heating, the process is not fully reversible with respect to temperature. Furthermore the temperatures necessary for removal of chemisorbed gas layers from the surface of a metal may be extremely high.

(b) Solution of hydrogen in the metal

Since absorption of hydrogen by steel is endothermic, then it is a true solution process. As was mentioned earlier, solubility was found to vary with $p_{H_2}^{1/2}$.

(c) Diffusion of hydrogen in iron and steel

Most of the theories which have been proposed in order to explain the mechanism of hydrogen embrittlement require the diffusion of hydrogen to some localized region of the lattice before its destructive effect becomes significant. Therefore some knowledge of the precise nature and rate of diffusion is of fundamental importance.

According to Seitz diffusion of hydrogen in iron occurs interstitially. Grain boundaries have been shown to have little or no effect on the diffusion process, since no difference
was detected. Although it is generally recognised that penetration of hydrogen into metals takes place in the atomic state there is still considerable controversy as to whether the hydrogen atoms are electrically neutral or ionized. Bastien has discussed this topic and considers that the available experimental evidence appears to favour diffusion at least partly in the form of protons.

Two main methods have been used to measure the coefficient of diffusion of hydrogen in iron and steel. The most widely used method, often referred to as the time-lag method, is the measurement of the evolution of hydrogen in vacuum from the inside walls of a cylinder, the external surface being exposed to gaseous hydrogen at varying temperature and pressure. This method has the disadvantage that diffusion data is derived essentially from 'permeability' data and, unfortunately, 'permeability' is due to a combination of adsorption, diffusion and evolution. Since permeability will obviously be affected by 'boundary' conditions (i.e. nature of the metal/gas or metal/solution interface) it is evident that great care is necessary in the interpretation of the results. Darken and Smith referred to the conditions which exist in this method (i.e. a constant rate of passage of hydrogen after a period of time, defined by the permeability constant, P) as the 'stationary state'.

in diffusion rate between single crystal and polycrystalline iron was detected.
A second method of measuring the diffusion coefficient entails measuring the rate at which a solid (usually cylindrical) steel specimen loses hydrogen when removed from the hydrogenation source. Darken used the term 'non-stationary state' to describe the conditions prevailing in this method.

More recent methods of measuring the diffusion coefficient of hydrogen in steel include the use of mass spectroscopy by Frank, Swets and Fry, and the use of an internal friction method by Hewitt.

Some typical values of D together with the respective methods of measurement are shown in Table 1.

The permeation of hydrogen through membranes and the desorption rate of the gas from hydrogenated samples have been frequently treated in terms of Fick's second law of diffusion, which for the linear case with constant diffusivity may be written:

$$\frac{\partial \sigma}{\partial t} = D \frac{\partial^2 \sigma}{\partial x^2}$$

where x is distance, t is time and \(\sigma\) concentration.

Thus Darken and Smith measured the rate and amount of hydrogen absorbed during acid pickling and concluded that this was consistent with the usual diffusion laws.
### TABLE 1

Values of diffusion coefficients for hydrogen obtained by various methods.

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<tr>
<th>Authors</th>
<th>$D$ (cm$^2$/sec)</th>
<th>Method of Measurement</th>
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<tr>
<td>Guntherschulze et al$^57$ (mild steel)</td>
<td>$5.5 - 11 \times 10^{-5}$ ($0^\circ C$) $8 \times 10^{-6}$ ($0^\circ C$)</td>
<td>stationary state (steady flow) time-lag</td>
</tr>
<tr>
<td>Stross and Tomkins$^58$ (pure iron)</td>
<td>$4.66 \times 10^{-6}$ ($20^\circ C$)</td>
<td>time-lag</td>
</tr>
<tr>
<td>Schuette and Robertsson$^4$ (armco iron)</td>
<td>$1 \times 10^{-7}$ ($20^\circ C$) $2 \times 10^{-6}$ ($20^\circ C$)</td>
<td>stationary state time-lag</td>
</tr>
<tr>
<td>Baranowski et al$^65$ (mild steel)</td>
<td>$5.0 \times 10^{-7}$ ($20^\circ C$) $9.6 \times 10^{-8}$ ($20^\circ C$)</td>
<td>time-lag (1st stage) time-lag (2nd stage)</td>
</tr>
<tr>
<td>Frank and Swets$^58$ (mild steel)</td>
<td>$5.0 \times 10^{-3} \exp [- \frac{3400}{RT}]$ $1.9 \times 10^{-2} \exp [- \frac{5320}{RT}]$</td>
<td>stationary state (mass spectrometry) time-lag (mass spectrometry)</td>
</tr>
<tr>
<td>Hobson$^60$ (forging steel)</td>
<td>$\sim 10^{-7}$</td>
<td>time-lag</td>
</tr>
<tr>
<td>Weiner and Gersamer$^89$ (mild steel)</td>
<td>$4 \times 10^{-4}$ $9 \times 10^{-5}$</td>
<td>stationary state (internal friction) time-lag (internal friction)</td>
</tr>
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</table>
Recently, however, considerable anomalies have been observed which appear to question the reliability of the application of Ficks' Laws to the diffusion of hydrogen in iron and steel. For instance, Baranowski et al. observed two distinct stages in hydrogen desorption from iron wires charged cathodically in acid solution at room temperature. They computed two values for the apparent diffusion coefficient for stages 1 and 2 respectively:

\[ D_1 = 5.0 \times 10^{-7} \]
\[ D_2 = 9.6 \times 10^{-8} \]

Later Hobson measured (in the temperature range -78 to 200°C) the rate of desorption of hydrogen from specimens cut from steel forgings. He observed that diffusion did not follow the accepted diffusion laws below approximately 130°C and obtained \( D \) values which were approximately 100 times less than those extrapolated from results of high-temperature measurement.

This apparent anomaly is discussed further in a later section.
2.6 Hydrogen absorption from aqueous solutions without applied e.m.f.

2.6.1 Pickling

A well-known example of hydrogen absorption with no applied e.m.f. occurs during pickling of steel in acid solutions. Darken and Smith carried out a systematic investigation of absorption and desorption of hydrogen by mild steel during and after immersion in acid solutions. The main conclusions arising from their work were:

(a) The amount of hydrogen absorbed was found to be related to the dimensions of the samples in the manner to be expected from the usual diffusion laws (this has already been discussed briefly);

(b) the amount of hydrogen absorbed increased linearly with the square root of time until a limiting concentration (the saturation concentration, \( c_s \), was reached;

(c) \( c_s \) was found to increase markedly with the extent of cold work;

(d) the effect of a decrease in acidity (increasing pH) on \( c_s \) was found to be small, but this factor had a more pronounced effect on the rate of absorption.

It is of interest to note that Zapffe has shown that whilst embrittlement of steel occurred readily during pickling in sulphuric, hydrochloric, phosphoric and hydrofluoric acids, only slight embrittlement was obtained with nitric acid. This is probably due to the fact
that nitric acid is highly oxidising and is able to act as a cathode reactant.

2.6.2 Influence of impurities

The rate of absorption and degree of embrittlement resulting from acid pickling has been found to depend markedly on the purity of the solution. Many elements have been found to promote entry of hydrogen into iron and steel and these are commonly known as 'poisons'. Early work by Aten et al \(^67\) established that arsenic and mercury behaved in this way and the elements selenium, tellurium, antimony, bismuth, and sulphur \(^68\) were later shown to behave in a similar manner. Occasionally the importance of possible catalytic poisons in hydrogen absorption and embrittlement studies has been overlooked; for instance, Brown \(^69\) used technical grade hydrochloric acid for pickling specimens.

The action of catalytic poisons has been ascribed to an increase in hydrogen overvoltage \(^70\) which is presumably due to the specific adsorption of atoms of the poisoning agent on the metal surface. Adsorption of hydrogen atoms or a subsequent intermediate step in the overall hydrogen evolution reaction is thus blocked by the poison. \(^44\) Smialowski \(^31\) considers that the ability of an impurity element to promote hydrogen absorption depends upon the bond energy of the hydride of this element. He points out that poisons are usually elements which form hydrides of relatively low bond energy, whereas oxygen and nitrogen which both form hydrogen compounds of greater stability than the hydrogen molecule itself, have no poisoning effect.

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Since sulphur compounds have been found to act as catalyst poisons when present in solutions, it might be expected that sulphur normally present in steel will also have an accelerating effect on hydrogen absorption, especially during pickling; this has been demonstrated by Sachs and Odgers. It has even been shown by some workers that high purity iron does not absorb hydrogen from pure acid solutions, whereas others claim that iron of similar purity does absorb hydrogen. Lack of knowledge of all of the factors involved in the introduction of hydrogen into steel may be the cause of this controversy.

2.6.3 Absorption from aqueous hydrogen sulphide

The phenomenon of stress corrosion of steel, especially high strength steels, in the presence of natural gas containing moist hydrogen sulphide has been the cause of great concern, particularly in the United States and France. Two groups of French and American workers have shown independently that this stress corrosion phenomenon is essentially a special case of hydrogen embrittlement and that considerable quantities of hydrogen can be absorbed by ferritic steels immersed in an aqueous solution of hydrogen sulphide. Bastien considers that hydrogen ions from the ionized hydrogen sulphide must diffuse into the metal since the presence of water appears to be a necessity for the occurrence of embrittlement; he has shown that no embrittlement
is produced when steel is immersed in a solution of hydrogen sulphide in a liquid with a much lower dielectric constant than water (i.e. benzene) in which ionization cannot occur.

Special steels with structures consisting of very fine uniformly distributed spheroidal carbide have been developed to counteract this particular stress corrosion hazard.

2.7 Hydrogen absorption from aqueous solutions with applied e.m.f.

2.7.1 Electrolytic charging

The technique of making the metal cathodic by means of an applied e.m.f. has been very widely used as a method of introducing hydrogen into steel specimens in order to study the resultant effect on mechanical properties. The method is considered by some authorities to be erratic; most likely this is due to complicating factors such as the variable poisoning effects of impurities and also surface finish of the specimens. It has been suggested by several workers that hydrogen introduced into steel by this method is not distributed evenly throughout the cross-section of the specimen, but that a high degree of hydrogen saturation occurs in a relatively thin surface layer.
2.7.2 Influence of current density on hydrogen absorption

The literature concerning the effect of current density on hydrogen absorption and embrittlement of iron and steel during electrolytic charging is beset with contradictions. Baukloh and Zimmerman using sulphuric acid reported a maximum in the rate of absorption by mild steel at a certain current density, above which the absorption rate decreased. The same workers using hydrochloric acid and a similar range of current density reported a steady increase in absorption rate with no maximum. Sachs and Melbourne used a slow bend test as a means of detecting embrittlement of mild steel screw wire cathodically charged in 10% by vol. hydrochloric acid. They showed that the effect of current density on ductility was negligible and that, provided a certain number of hydrogen atoms were supplied to unit area of the surface, increasing the rate of hydrogen discharge did not affect the embrittlement process. It is considered that this work would have been more significant if the hydrogen content of the steel had been determined in conjunction with the mechanical tests.

Further results which conflict with those of Sachs and Melbourne have been reported by Phelps and Loginow, who investigated the effect of cathodic polarization on the average cracking time of high-strength steel subjected to a static bend test whilst
immersed in aerated 3% sodium chloride. At low cathodic current densities they found that time to failure was greatly increased over that obtained with no polarization; at higher current densities time to failure became progressively shorter.

Schuetz and Robertson determined the effect of current density on the saturation concentration \( (c_0) \) of hydrogen in a martensitic steel using cathodic charging in sulphuric acid containing arsenic. They found that the data obtained conformed with a relationship of the following form:

\[
c_0 = a + b \log i
\]

where \( c_0 \) is the saturation concentration, \( i \) is current density, and \( a \) and \( b \) are constants.

There is a striking similarity between this equation and the Tafel equation relating overvoltage and current density for hydrogen evolution. The reproducibility obtained in this work, in common with other studies of hydrogen absorption from acid solutions, was not very good.

Data available on the effect of cathodic polarization on the rate of hydrogen absorption (as measured by an analytical method) is scarce and much more information is required concerning this aspect. Especially lacking is data relating to the possibility of hydrogen embrittlement of steel due to sacrificial galvanic protection. This is discussed later in the appropriate section.
2.7.3 **Embrittlement resulting from electroplating**

The brittle failure of components following electroplating is well known; furthermore, it is recognised that the ductility of electroplated components which have absorbed hydrogen can be restored to their initial safe level by an ageing or baking treatment at elevated temperatures. Some metals (e.g. cadmium) are impermeable to hydrogen and the gas is considered to escape through pores in the coating. Recent work by Brown however, has shown that baking treatments are not so effective when the U.T.S. of the steel is greater than 90 tons/in$^2$.

Hydrogen embrittlement is of particular significance with respect to steels plated with cadmium from the conventional cyanide bath. Efforts to develop cadmium plating processes to counteract embrittlement include cadmium plating from a fluoborate bath,\(^{69}\) the addition of various organic compounds to the conventional plating bath\(^ {81,84}\) and the two-stage plating process described by Troiano.\(^ {85}\) In the latter technique flash plating followed by baking and then plating to full specification is claimed to produce satisfactory embrittlement-free plated components, but some doubt exists on this point. It does not appear convincing, for instance, that if the initial flash deposit will allow hydrogen to pass outwards during baking, further passage of hydrogen into the metal will not occur during the final plating treatment.
2.8 Relationship between hydrogen embrittlement and metallurgical condition of the steel

It is generally agreed that the higher the U.T.S. of steel the greater is the effect of hydrogen in causing loss of ductility; this has been clearly demonstrated by Frohmberg et al.\textsuperscript{25} It seems surprising, therefore, that the same workers found that notched specimens of high-strength steel of different U.T.S. behaved similarly under sustained load conditions. Very high-strength steels (medium carbon, low alloy) are usually obtained by quenching followed by moderate tempering; the metallurgical structures obtained at medium and low tempering temperatures are not particularly stable. Bastien\textsuperscript{50} showed that the more thermodynamically stable the structure the less the susceptibility to hydrogen embrittlement - structures consisting of pearlite, bainite or fine spheroidal cementite in a ferrite matrix should be least affected by hydrogen, while martensite structures which contain high internal stresses would be most affected. Presumably partially tempered structures lie in between these two extremes, although Smialowski\textsuperscript{31} showed from simultaneous cathodic charging and applied tensile stress experiments that a marked improvement in sustained-load properties of a medium C structural steel was obtained after hardening and tempering at 300°C.
Considerable differences of opinion appear to exist with regard to the relative absorbing powers of different metallurgical structures for hydrogen. For instance, Bastien showed that under similar experimental conditions fine spheroidised structures absorb much less hydrogen than martensitic structures. In contrast Schuetz and Robertson reported that the saturation concentration \( c_s \) of hydrogen in a martensitic nickel/iron alloy hydrogenated by cathodic charging in sulphuric acid was similar to that obtained in a ferritic nickel/iron alloy of the same composition. They did find, however, that the absorption rate was greater for martensite than ferrite and they consider that this accounts partly for the greater susceptibility of martensite to embrittlement.

A certain degree of controversy is also apparent in data reported on the effect of cold work on hydrogen absorption. Darken and Smith found that during hydrogen absorption from sulphuric acid the saturation concentration for mild steel increases in proportion to the amount of cold work up to 75% reduction. Schuetz and Robertson, however, reported a minimum in \( c_s \) for a 10% nickel/iron ferritic alloy at approximately 30% reduction. Schumann and Erdmann-Jescnitzer have obtained results on plain-carbon steel in agreement with those of Schuetz and Robertson.
2.9 Hydrogen absorption and embrittlement due to sacrificial protection

The general nature of this problem was outlined in the introduction to the present section. Whilst the main protective action of cadmium and aluminium coatings is derived from physical exclusion of corrosive agencies from the steel substrate, it is almost inevitable that pores and discontinuities will exist in these coatings. Some doubt exists as to whether it is feasible for hydrogen to enter the cathodically polarized steel at these points and migrate to some favoured lattice site until eventually the critical concentration necessary for embrittlement is exceeded.

A complete investigation of this aspect of hydrogen embrittlement does not appear to have been attempted and the relatively small amount of data that is available in connection with the problem does not help to clarify the situation. Uhlig for instance has demonstrated that it is actually possible to cause embrittlement under such conditions, at least with a steel of the 12% Cr martensitic type. He has shown that rapid failure of such a steel can be made to occur by coupling it with aluminium whilst it is simultaneously subjected to an applied stress and immersed in 3% sodium chloride. Certainly if embrittlement by this process was even remotely possible it should be manifested in martensitic-type steels which are known to be particularly susceptible to hydrogen embrittlement. On the other hand, however, Phelps and Loginow...
have reported that specimens of a similar steel protected by a sprayed aluminium coating did not fail in atmospheric stress-corrosion tests carried out in a very corrosive seawater-spray environment.

In complete contrast to the numerous studies carried out in acid solutions very little information on the kinetics of hydrogen absorption by high-strength steels from near-neutral solutions (i.e. pH 4 to 9) appears to be available. Furthermore, although the mechanisms of the hydrogen evolution reaction in both strongly acid and strongly alkaline solutions have received a good deal of attention the situation in the intermediate pH region is much less satisfactory. In particular, very little work appears to have been carried out involving carefully controlled experiments where both the hydrogen evolution and absorption processes have been studied simultaneously. Reference has already been made to the fact that hydrogen absorption and embrittlement have often been evaluated solely by mechanical tests and that little attention has been given to the accurate quantitative determination of amounts of hydrogen absorbed.

With these considerations in mind it was felt that a study of factors influencing hydrogen absorption of high strength steels during cathodic polarization in solutions of intermediate pH would be of interest. Cathodic polarization in near-neutral solutions
would tend to simulate the possible conditions operative in service when steel is coated with a galvanically less noble metal. A study of this problem has therefore been undertaken using a sensitive analytical technique for quantitative determination of hydrogen in steel.

In general the effect of the following factors on hydrogen absorption of cathodically polarized high strength has been studied:

1. pH of the solution (in the range 4 to 9)
2. duration of polarization
3. electrode potential of the steel
4. metallurgical condition of the steel
5. impurities in the solution.
SECTION 3. EXPERIMENTAL PROCEDURE

3.1 Specimen Preparation

3.1.1 Materials used

The high strength steel used for the investigation was an experimental Firth Brown low alloy steel (REX.539). Both 0.375 in. diameter rod and 0.2 in. thick sheet were available. A typical analysis was as follows:

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>1.50</td>
<td>1.50</td>
<td>0.02</td>
<td>0.02</td>
<td>1.75</td>
<td>0.40</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The residual hydrogen content measured by solid state vacuum extraction was in the range 0.06 - 0.10 p.p.m. hydrogen. Details of the extraction procedure used are given in Sections 3.3.2 and 4.2.

A limited number of experiments were performed with spectrographically standardised iron rod (impurities < 0.001%) in the annealed condition (1 h. at 800°C in vacuum). This was found to have a much higher residual hydrogen content than the REX.539 material (of the order of 1 p.p.m.).

3.1.2 Heat-treatment

By selection of suitable heat-treatment procedures REX.539 steel cylindrical specimens were obtained in a variety of metallurgical conditions. The conditions investigated and the procedure used to achieve the desired structure are summarised in Table 2.
<table>
<thead>
<tr>
<th>Type of Microstructure</th>
<th>Heat-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>martensite</td>
<td>Austenitized 860°C (1h), oil-quenched</td>
</tr>
<tr>
<td>partly tempered</td>
<td>Austenitized 860°C (1h), oil-quenched</td>
</tr>
<tr>
<td>martensite</td>
<td>tempered 100°C - 400°C (1h)</td>
</tr>
<tr>
<td>very fine spheroidal</td>
<td>Austenitized 860°C (1h), oil-quenched,</td>
</tr>
<tr>
<td>Fe₂₃C in ferrite matrix</td>
<td>tempered 600°C (1h)</td>
</tr>
</tbody>
</table>
Austenitizing of specimens prior to transformation was performed in a conventional electrical resistance furnace (Fig.1) with a furnace atmosphere of pure argon previously dried by passing through concentrated sulphuric acid. The temperature was controlled to within ± 5°C by means of an Ether 'Transitrol' indicating temperature-controller (type No. 991G).

All tempering treatments were carried out in vacuum; the heating section of the hydrogen extraction apparatus (Fig.10) was utilized for this purpose. Tempering in vacuum has the advantage that any readily diffusible hydrogen in the specimen is removed during the tempering operation (see Section 4.2). Tempering at 600°C in vacuum will also remove most (perhaps all) of the residual hydrogen present. Since the level of residual hydrogen in the REX.539 material is extremely low, the latter point is of relatively minor significance.

3.1.3 Preparation of specimen surface

In view of the observation by Duflot\textsuperscript{77} that the condition of the steel surface has a marked effect on hydrogen absorption by steel, it was considered extremely important to adopt a carefully standardised final surface preparation procedure for all specimens. In general two methods are available for final surface polishing. They can be classified as follows:
ARGON IN

SULPHURIC ACID

FURNACE TUBE

OUT

THERMOCOUPLE

HEAT-TREATMENT APPARATUS

FIGURE 1
(a) methods relying on chemical or electrochemical treatments (e.g. chemical polishing, electropolishing),
(b) mechanical polishing methods.

Although the type of surface finish obtainable by group (a) methods is superior for electrochemical studies, it was decided to avoid such methods for two reasons. Firstly, they involve the risk of premature introduction of hydrogen into the steel specimens prior to polarization studies. Secondly, electropolishing invariably leaves a film on the surface of the specimen. Chemical polishing using Marshall's solution (oxalic acid 2.5 g/100 ml; hydrogen peroxide 1.3 g/100 ml; sulphuric acid 0.01 g/100 ml) was attempted, but although good results were obtained with pure iron the method was found to be unsuitable for the low-alloy type of steel used since a black smut was formed on the surface. It was thus decided to adopt a procedure based on light mechanical abrasion with a range of silicon carbide papers followed by polishing with coarse and fine Hyprez diamond compound. Where possible a low-temperature stress relief treatment (1 h at 200°C in vacuum) was carried out after final polishing in order to remove residual surface stresses as completely as possible.

The full details of specimen preparation procedure are summarised below:
1. Machine to 0.200 in. dia. and 1 in. length (+ 0.015 in. oversize).
3. Grind to final size.
4. Lightly abrade with range of silicon carbide papers and polish with coarse and fine diamond compound, finishing with \( \frac{1}{2} \mu \) particle size diamond.
5. Stress-relieve (if possible) for 1 h at 200°C in vacuum.
7. Dry in hot air blast.

3.1.4 Mechanical properties

Several specimens from each batch were checked for tensile strength by determining the hardness by means of the Vickers diamond pyramid indentation hardness method and applying the relevant conversion factor (0.21). Typical results for the various metallurgical structures studied are shown in Table 3.

A limited number of miniature tensile tests were also performed with a Hounsfield Tensometer, and the results of these are also included in Table 3.

The agreement between the two methods was excellent.
### TABLE 3

**Dependence of U.T.S. of REX 539 on heat-treatment**

<table>
<thead>
<tr>
<th>Structure</th>
<th>U.T.S., ton/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V.P.N. method</td>
</tr>
<tr>
<td>Martensite</td>
<td>142</td>
</tr>
<tr>
<td>Martensite tempered at 200°C</td>
<td>138</td>
</tr>
<tr>
<td>Martensite tempered at 400°C</td>
<td>132</td>
</tr>
<tr>
<td>Very fine Fe₃C in ferrite matrix (tempered at 600°C)</td>
<td>85</td>
</tr>
</tbody>
</table>
3.2 Electrochemical Techniques

3.2.1 Design of cell for polarization studies

When considering the design of a cell for the present study the following characteristics were considered to be important:

(a) The cylindrical steel specimen should be mounted in such a way that the potential at its surface could be measured easily and accurately with a reference capillary - the maximum possible surface area of the specimen should be exposed to the electrolyte solution. Also removal of the specimen after polarization should be accomplished easily and with minimum loss of time without the necessity of draining the electrolyte and dismantling the cell.

(b) Continuous removal of dissolved oxygen from the electrolyte throughout the course of polarization by out-gassing with an inert gas stream was considered to be essential in order to achieve reproducible results for hydrogen absorption. Depolarization of the hydrogen evolution reaction would thereby be avoided thus ensuring that the only possible cathodic reactions involving hydrogen ions would be absorption of hydrogen by the cathode and formation of molecular hydrogen (which will either dissolve in the electrolyte solution or evolve as gas bubbles.)
(c) The anode should be situated in a separate compartment at a suitable distance from the cathode consistent with cell resistance considerations. Precautions should be taken to ensure that oxygen evolution at the anode does not result in oxygen dissolving in the solution and reaching the cathode — this was achieved by out-gassing of the analyte with a stream of oxygen-free argon. It should be noted that this precaution was unnecessary in later experiments in which a hydrogen electrode was employed as an anode. (Section 2.2.5)

(d) Concentration overpotential in the vicinity of the cathode should be minimized — this was achieved by agitation with a high velocity gas stream.

(e) It was desirable to avoid using all materials other than borosilicate glass, polytetrafluorethylene (P.T.F.E.) and clear P.V.C. tubing in construction of the cell and handling of solutions in order to minimize introduction of impurities into the electrolyte. The deleterious effect of impurities on the hydrogen evolution reaction has been discussed by Bockris and also by Potter.
The design ultimately adopted for the present study is shown in Figs 2 and 3, and consisted of a cell having a capacity of approximately 350 ml with the following features:

1. Cathode compartment A,
2. anode compartment B,
3. reference probe G mounted in parallel-sided ground glass joint F leading to reference electrode E,
4. parallel-sided ground glass joint P supporting cathode C,
5. cell base L,
6. side-tube M.

The cylindrical steel cathode C was mounted in its supporting ground-glass joint P by means of a P.T.F.E. sleeve H, with the minimum possible surface area shielded by the P.T.F.E. This design enabled rapid withdrawal of the cathode from the cell to be carried out easily prior to quantitative determination of absorbed hydrogen. Electrical connection was achieved by a length of pure iron wire which was in pressure contact with the specimen.

The potential of the cathode C was measured by means of a Luggin capillary G mounted in a ground-glass joint F. By means of this joint it was possible to position the capillary tip at any
FIGURE 2

Photograph of electrochemical polarization cell
desired distance from the cathode. In early experiments actual contact with the cathode invariably resulted in entrainment of a hydrogen bubble in the capillary tip thereby interfering with potential control in potentiostatic experiments and potential measurements in galvanostatic experiments. It was therefore necessary to maintain a fixed distance (usually 1 mm) between the capillary tip and the cathode surface. Except at high current densities the resultant 1R drop across the intervening electrolyte was found to be negligible.

The ground-glass joint F supported the reference electrode by means of a 'Quickfit' B14 socket. Diffusion of chloride ions into the reference capillary and hence into the cathode compartment was restricted by a sintered glass disc N. In later experiments, however, it was suspected that diffusion of chloride ions from the reference electrode into the cell was occurring and interfering with results (Section 3.2.5); consequently the calomel electrode was replaced by a mercury/mercurous sulphate reference electrode (Section 3.2.4).

Cathode and anode compartments were both provided with sintered glass discs J, K respectively, through which a high velocity inert gas stream (purified argon) was injected into the electrolyte prior to and during polarization. All 'Quickfit' joints and the cell drainage tap were maintained free from grease, which would other
wise interfere with electrode processes. Electrical connection
to the platinised platinum anode D was achieved by means of a
mercury contact R. A special procedure for deoxygenating the
electrolyte and filling the cell by means of side-limb M was adopted.
This is described in Section 3.2.3.

3.2.2 Thermostat
All polarization experiments were carried out in an
enclosed air thermostat chamber heated by a 100 watt light bulb and
maintained at 25°C ± 0.5°C by means of a simple xylene expansion
thermometer and a make-and-break mercury contact relay. Air circu-
lation was maintained by means of a small electrically-driven fan.

3.2.3 Solutions
The selection and handling of solutions for polarization
studies was governed by several important factors:

1. It was essential that only solutions of high purity
should be used. Particular care was taken to ensure
that all reagents used in the preparation of solutions
were as free as possible from elements which would either
specifically promote or hinder the entry of hydrogen
into steel. Analar chemical reagents were found to be
satisfactory in this respect, and all distilled water
for solution preparation was first re-distilled in an
all-borosilicate glass apparatus.
2. The importance of adequately controlling the pH of solutions during polarization experiments was recognised. Buffered solutions were therefore employed for the majority of experiments. Mixtures of 0.2 M sodium acetate/0.2 M acetic acid were used for pH values in the range 4 – 6; for higher pH values (8 – 10) sodium borate/boric acid solutions were used.

3. It was realised that dissolved oxygen in solution would lead to depolarization of hydrogen evolution (and presumably also hydrogen entry) reactions. Since the precautions outlined in (1) did not exclude dissolved oxygen from solutions, special consideration was given to its removal before electrochemical experiments, and to preventing re-entry into the solution during polarization. The latter problem has already been mentioned in describing the polarization cell. (Section 3.2.1)

Fig. 5 is a diagram of the arrangement adopted for de-oxygenating solutions prior to polarization. The solution was first poured into the modified 'Nilox' scrubber (Southern Analytical Ltd.) and isolated from the air. Taps T1, T3 were then closed and T2, T4 opened to allow pure argon into the system. Trace amounts of oxygen in the argon were first removed by passing the gas through
DE-OXYGENATED ARGON OUT

ARGON IN

GAS SCRUBBER

FIGURE 4
the 'Nilox' scrubber illustrated diagrammatically in Fig. 4. The scrubber contained chromous sulphate solution, to which 1 ml of a surface-active agent (Lissopol) had been added, and a bed of amalgamated zinc. As argon entered the base of the spiral tube, small bubbles of the gas were entrained in the solution and travelled to the top of the spiral. The flow of argon thus led to a continuous re-circulation of chromous sulphate solution up the outer spiral and down through the main body of the scrubber. Since chromous salts are easily oxidised to the trivalent state, any trace amounts of oxygen present in the argon are effectively reduced to water. The Lissopol assisted in promoting smaller gas bubbles thereby giving greater surface contact area between the argon and the solution in the spiral and facilitating rapid and efficient de-oxygenation. The slightly oxidised solution was quickly reduced to the original divalent state on passing downwards through the zinc amalgam.

On leaving the top of the scrubber purified argon flowed through tap T₂ (Fig. 5) to the base of an identical scrubber containing the solution to be de-oxygenated. Circulation of this solution around the scrubber was thus effected in the same way as in the first scrubber. Gilroy and Mayne have shown that this method of removing oxygen from solutions is far more efficient than conventional techniques involving flushing with an inert gas stream.
After leaving the top of the second scrubber, argon passed through tap T4 and hence to the base of the polarization cell. This was continuously flushed with argon via the sintered glass disc J (Fig. 3) and the gas finally passed out of the system through a water seal.

After allowing the solution to re-circulate for approximately one hour, taps T1, T3 were opened; tap T2 being simultaneously closed; tap T4 was allowed to remain open. This operation reversed the flow of argon (i.e. argon now entered the top of the scrubber through T3). The gas continued to flow through T4, however, and hence into the cell. Pressure build-up of argon in the scrubber forced the solution to flow out along the path shown in Fig. 15 (Operation 2) and into the cell via side-limb M. Contact with air was thus avoided until argon was bubbling through the solution, which was then ready for use in polarization experiments.

3.2.4 Reference Electrode

A 0.1 N calomel half-cell (E = 0.334V) was employed as reference electrode in early experiments. It was later suspected, however, that chloride ions were diffusing into the main cell compartment and interfering with the cathodic reaction as described in Section 3.2.5. A saturated mercury/mercurous sulphate half-cell (E = 0.618V) was therefore used in subsequent experiments.
The relatively appreciable solubility of mercurous sulphate (compared with mercurous chloride) is thought to assist in promoting very efficient depolarization, thus helping to make this electrode highly reproducible.

3.2.5 Selection of anode

The selection of a suitable anode for the polarization cell (Fig.3) was governed by two important factors. Firstly, it was desirable, if possible, to avoid evolution of oxygen at the anode and its diffusion to the cathode where it would become reduced in preference to hydrogen ion reduction and thus affect hydrogen entry into the steel cathode. Evidence of interference of hydrogen absorption by oxygen is presented in a later section (Section 4.3.3). Secondly, it was extremely important to avoid introducing impurities into the solution from the anode; the adverse effect of impurities on the hydrogen evolution and hydrogen entry reactions has already been mentioned. For this reason consumable types of anode (e.g. magnesium, zinc) were considered undesirable, even if they were of higher purity.

In early experiments an anode consisting of a simple platinum foil was used and since oxygen evolution was unavoidable, a high-velocity inert gas stream (pure argon or nitrogen) was directed over the anode surface by means of a sintered glass disc (K, Fig.3).
With a platinum anode there was also the danger that if chloride ions were present in the solution, chlorine evolution might occur at the anode. This would probably result in the formation of hypochlorite ions in solution, which would also interfere with cathodic reduction of hydrogen ions. Since a 0.1 N calomel electrode was employed as a reference electrode in early experiments it was possible for small amounts of chloride ions to enter the main cell compartments via sintered glass disc N and capillary G. An alternative anode was therefore sought, and subsequently a large hydrogen electrode was chosen. With this type of anode the only possible reaction (especially at the low current densities employed in the present studies) was oxidation of hydrogen gas to hydrogen ions; provided a buffered solution was used, little or no change in pH could result from this reaction.

The hydrogen electrode is normally used as a reference electrode, and consists essentially of a platinized-platinum electrode immersed in a solution containing hydrogen ions and saturated with hydrogen gas. The electrode was prepared in the following way:

A piece of platinum foil, spot-welded to a short length of platinum wire which was sealed into a glass tube, was prepared so that an area several hundred times the geometrical area of the foil was in contact with the solution. This was achieved by electro-
deposition of finely divided platinum onto the foil from a 2% solution of chloroplatinic acid, $\text{H}_2\text{PtCl}_6$, in normal hydrochloric acid, using a platinum anode. Both electrodes were first cleaned by immersion in warm aqua regia for 10 s followed by rinsing with distilled water. A current of 0.1 A/cm$^2$ of cathode area was then applied for approximately 30 min. A smooth adherent black deposit of finely divided platinum formed on the cathode, which was then rinsed thoroughly and stored in distilled water.

The electrode was set up as shown in Fig. 3 (anode compartment, B). The sintered glass disc, K, was used to bubble a slow stream of pure hydrogen gas through the anode compartment, B. Excess hydrogen was led away from the cell by a side-arm.

3.2.6 Potentiostatic studies

The circuit diagram for potentiostatic experiments is given in Fig. 6. The potentiostat used was supplied by Witton Electronic Ltd. to specification, and had a maximum sensitivity of 1280 mA/V in the operating range of 10 mA, with identical reverse behaviour. The sensitivity was such that at currents of $\leq$ 1 mA the fluctuations were less than 1 mV; in the range 1 - 10 mA, fluctuations of $\leq$ 5 mV were usually obtained.
CIRCUIT DIAGRAM FOR POTENTIOSTATIC STUDIES

VALVE

VOLTOMETER

CELL

mA

POTENTIOSTAT

REFERENCE TEST PLATINUM

LOW

HIGH
A potentiometer was unsuitable for measurement of potentials in conjunction with a potentiostat as, when operated even slightly off balance, a back e.m.f. was forced through the potentiostat and affected its stability. It was, therefore, necessary to employ an instrument having a high impedance, and a valve voltmeter (Electronic Instruments Ltd., model No. 26) was found to be suitable. Cell currents were measured with a substandard multi-range ammeter (Weston, type S 82).

3.2.7 Galvanostatic supply

The circuit diagram employed for galvanostatic experiments is shown in Fig.7. An electronic constant current device (Solartron model) was used in series with a number of variable wire-wound resistors. Potential and current measurements were performed as described in Section 3.2.6, although the galvanostatic circuit was amenable to replacement of the valve voltmeter by a potentiometer.
3.3 Determination of Absorbed Hydrogen

3.3.1 Survey of methods available

Introduction

It was well known to early workers\(^{94}\) that large quantities of hydrogen could be evolved from iron or steel which contained hydrogen by simply heating the metal. It was also realised that evolution could be speeded up by lowering the partial pressure of hydrogen around the heated steel specimen;\(^{95}\) this could be achieved by continuous evacuation of the furnace tube containing the specimen. Quantitative measurement of the hydrogen content was unreliable, however, because of the uncertainty of complete removal of hydrogen from the steel. Improvement in vacuum techniques in the 1930's enabled vacuum melting of steel to be achieved thus ensuring rapid and complete removal of dissolved gases. Thus, interest in the accurate quantitative determination of hydrogen in metals received a fresh stimulus.

The chief methods which have been utilized for extraction of hydrogen from steel are as follows:

\((c)\) vacuum fusion (molten metal)

\((b)\) vacuum extraction (solid metal)

\((c)\) carrier-gas techniques.
Vacuum fusion

In this technique the sample is melted (or alternatively dissolved in a molten metal of much lower melting point) in a graphite crucible at a temperature of 1500 - 2000°C in vacuum. The primary purpose of this procedure is to convert the dissolved (or combined) oxygen to carbon monoxide and thus determine the oxygen content of the metal. Nitrogen and hydrogen, if present, are also evolved and the gases present in the system can be analysed by a suitable means. The disadvantages of this method as a means of only determining hydrogen are that the apparatus used is complex and requires several hours de-gassing before determinations can be carried out. Also the hydrogen evolved is normally only a small fraction of the total gas and therefore accuracy may not be high. Furthermore, owing to the high temperatures involved 'blank' errors are often difficult to overcome, although the use of a tin bath, in which the steel is dissolved, enables the use of a much lower temperature (1100°C) and consequently reduces the 'blank' rate. Carney et al., for instance, were able to achieve an accuracy of 0.1 p.p.m. using this latter technique.

Quantitative analysis of the amount of hydrogen present was achieved in the past by transferring the gas to a conventional Orsat or Ambler type gas analysis apparatus and making volume
measurements at or near atmospheric pressure after absorption or combustion of each gas in turn. Gravimetric methods involving combustion of the gas and absorption of the gaseous combustion products, followed by weighing, have also been used. These methods will not usually detect less than 1 p.p.m. hydrogen and are, therefore, of little use for lower hydrogen contents. A more recent and more accurate means of measuring hydrogen is to separate the gas by means of a palladium tube. This is discussed more fully in Section 3.3.2.

More recently still, the techniques of gas chromatography and mass spectroscopy have both been applied to analysis of the gases extracted by vacuum fusion.

Vacuum extraction (solid state)

The development of the vacuum fusion method for determining oxygen, nitrogen and hydrogen in steel provided a means of assessing whether or not heating of a hydrogen-containing steel specimen in vacuum would give complete evolution of hydrogen without the necessity of melting the metal. Sloman and Newell subsequently showed that complete extraction of hydrogen could be achieved at temperatures of around 600°C in about 30 min for a \( \frac{1}{2} \) in. dia. sample. Moreover, they showed that the gas extracted at this relatively low temperature was almost 100% hydrogen.
Several advantages of using vacuum heating rather than vacuum fusion for determining hydrogen in steel are immediately apparent:

(a) Because of the relatively low temperatures involved there is little difficulty in obtaining a good apparatus 'blank'.

(b) The apparatus required for vacuum extraction is simpler than that needed for vacuum fusion. A small resistance furnace with a silica tube can be used to heat the specimens.

(c) Conditions can often be arranged so that the extracted gas is pure hydrogen containing no other gases.

Provided that condition (c) can be achieved the need for analysis of the extracted gas after every determination does not arise. The use of a means of measuring the actual amount of hydrogen present is an advantage, however, and this is apparent from the results of preliminary experiments which were carried out to ascertain the most suitable temperature for extraction in the present work. (Section 4.2).

The methods available for detection and measurement of hydrogen are similar to those mentioned for the determination hydrogen extraction by vacuum fusion.
Carrier-gas techniques

It was recognised quite early\(^{104}\) that one of the main conditions necessary for complete removal of hydrogen from steel (i.e. lowering of the partial pressure of hydrogen around the specimen) could theoretically be achieved by the use of a streaming carrier gas as well as by vacuum techniques. Such a method has several advantages over vacuum methods, at least for routine production analysis. For instance, the method can be operated at atmospheric pressure thus obviating the need for expensive and often troublesome vacuum equipment. Continuous-gas flow methods, however, appear to suffer from the disadvantage that the apparatus 'blank' rate is difficult to control to a very low level; this makes the determination of hydrogen to a precision of \(\pm 0.01\) p.p.m. by this technique virtually impossible at present.

An example of a carrier-gas technique is the method of estimating hydrogen developed by Coe and Jenkins.\(^{105}\) Argon, which is employed as the carrier gas, is swept over the heated specimen; a thermal conductivity cell (or katharometer) is used to determine the quantity of hydrogen in the argon gas stream. However, the estimated precision of the method is only \(\pm 0.04\) p.p.m.

An excellent review of carrier-gas methods for determination of hydrogen in metals has been compiled by Shanahan.\(^{106}\)
Other techniques

An isotopic equilibration method has been proposed by Zaidel and Petrov. In this technique the sample is heated in an enclosure and allowed to come to equilibrium with a gaseous mixture containing known quantities of hydrogen and deuterium. Zaidel and Petrov assumed, perhaps unjustifiably, that hydrogen and deuterium are equally soluble in the metal; thus they postulated that hydrogen in the sample and deuterium in the gas would distribute themselves in the same way between the gas phase and the sample and, therefore, by measuring the final amount of deuterium in the gas phase the hydrogen content could be calculated.

The technique of ionic bombardment in which the sample is made the cathode in a gas discharge running in a moderate vacuum, and the evolved gas is collected and analysed, has been examined by Bobalek and Shrader as a possible means of determining hydrogen in metals. They concluded, however, that the method was both difficult and inconvenient.

There are a few types of physical measurement which can be made specific to hydrogen but which have not as yet been utilized for analytical determination. Damping capacity (internal friction) appears to be promising in this respect. The use of emission spectroscopy is currently being studied as a possible means of determining hydrogen in metals.
3.3.2 Design and operation of apparatus

From the preceding review of available methods it would appear that the most reliable method for quantitatively determining small amounts of hydrogen (0.05 - 0.5 p.p.m.) is the well-established solid state vacuum extraction technique. Accordingly an apparatus based on this principle was designed and constructed for the present investigation.

Description of apparatus

A line diagram depicting the general features of the apparatus is shown in Fig. 9; Figs. 10, 11 and 12 show individual sections in more detail; a general photograph is also included (Fig. 8).

The extraction section comprised a silica tube B having a recess tube in which a chromel/alunel thermocouple T (Fig. 10) is housed, a small resistance furnace A, a mercury column C and reservoir 0, and a mercury vapour diffusion pump D (Edwards High Vacuum, Model GM.2, giving an ultimate vacuum of approximately $10^{-6}$ mm Hg.) The temperature of the resistance furnace was controlled to ± 5°C by means of an Ether 'Transitrol' indicating temperature-controller (Type No. 991G). The mercury column and reservoir were so designed that a 3 in. length specimen could be introduced directly into the previously evacuated apparatus.
FIGURE 8

Photograph of hydrogen analysis apparatus
DIAGRAM OF VACUUM EXTRACTION APPARATUS FOR HYDROGEN DETERMINATION

FIGURE 9
VACUUM EXTRACTION APPARATUS —
COLLECTION AND PRESSURE MEASUREMENT SYSTEM

FIGURE 11
VACUUM EXTRACTION APPARATUS — HYDROGEN MEASUREMENT SECTION
Since it is well known that hydrogen is lost quite rapidly from ferritic steels at room temperature, large errors would occur if specimens were not analysed for hydrogen immediately following polarization; hence the need for some form of air-lock device to permit insertion of specimens into the already evacuated apparatus. A mercury lift device was introduced for this purpose by Derge, Peifer and Alexander \(^{110}\) in 1945 and has since proved very popular. Unfortunately, the technique suffers from the disadvantage that small amounts of adsorbed water vapour appear to be introduced into the apparatus along with the specimen and can lead to errors in analysis, particularly where hydrogen contents of the order of 0.10 p.p.m. are being determined (reference should be made to Section 4.2 for a more detailed account.)

The mercury vapour diffusion pump performs the dual role of evacuating the apparatus and confining hydrogen evolved from the heated sample to the collection and pressure measurement system of the apparatus (shown in detail in Fig. 11). Basically the collection system comprised a 250 ml volume E, three smaller accurately calibrated volumes \((V_1, 15 \text{ ml}; V_2, 3 \text{ ml}; V_3, 0.23 \text{ ml})\) and an adequately supported mercury reservoir, F. A two-way stop-cock \(T_1\), connected the upper part of the reservoir to the backing pump during normal operation. By turning \(T_1\) to the atmosphere and carefully allowing air to enter F by means of a needle
valve, N, mercury rose and any gases in the system were confined into the calibrated volumes $V_1, V_2, V_3$ in this way. A valve, G, consisting of a small steel cylinder sealed into a glass seating prevented mercury from rising beyond G in limb L. A metre rule allowed measurement of the head of mercury in limb M, due to compression of the gas in the calibrated volumes. A Pirani gauge head, J, (Fig.9; Edwards High Vacuum, Type G6) connected to a Pirani-Penning gauge unit (Edwards High Vacuum) enabled the progress of hydrogen extraction from the sample to be followed continuously. A liquid-air-cooled limb, H, (Fig.9) was included to condense out any water vapour present in the system.

The hydrogen measurement unit is shown diagrammatically in Fig.12. A palladium tube, P, was gold-soldered to a short length of platinum tube, S, which was in turn sealed to soda glass and hence to pyrex glass by a graded glass seal, U. A small resistance furnace, R, controlled by a Variac (Zenith Electrical Co., Model No.10CRM) was used to heat the palladium tube, current connections being made by means of tungsten wire sealed into the auxiliary vacuum system surrounding the palladium tube unit. Palladium is readily permeable to hydrogen at 450 - 600°C and when the collected gases are allowed to come into contact with the inside surface of the palladium tube hydrogen can be removed from the system very rapidly. Three important precautions must be observed in order to achieve satisfactory results with this method.
Firstly, palladium must not be thermally cycled whilst in contact with hydrogen, since this apparently results in rapid physical deterioration of the metal. This difficulty has recently been offset by the development of a palladium/silver alloy\textsuperscript{111} which possesses excellent hydrogen permeation characteristics without danger from physical deterioration. Secondly, whilst diffusion in a gas mixture is extremely rapid at low pressures (e.g. $< 0.1 \text{ mm mercury}$) at higher pressures it may be a limiting factor and all of the hydrogen may not reach the palladium tube, thereby giving rise to a false apparent end-point. It is possible to overcome this by arranging for the gases to circulate continually over the palladium thimble. This difficulty did not arise in the present investigation because of the small amounts of hydrogen encountered. Thirdly, if other gases besides hydrogen are present in the system, reactions leading to the production of additional spurious hydrogen at the hot palladium surface are possible, e.g.

$$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$$

This can be avoided by employing a liquid air cooled limb. It is extremely unlikely, however, that carbon monoxide was present at the comparatively low extraction temperatures used in the present work. (Section 4.2).
It should be mentioned that the hydrogen extraction and measurement apparatus was constructed entirely of silica or glass (apart from the palladium tube) in order to avoid the possibility of sorption of hydrogen on metal surfaces. Furthermore, the number of stop-cocks in the system was kept to the absolute minimum and high grade vacuum grease (Edwards apiezon T-grease, or, alternatively, a softer grade grease) was used on all stop-cocks. The whole system (including the two auxiliary vacuum chambers) was evacuated by an Edwards rotary backing pump, (Model No. ISP30B, Z, Fig.9).

**Operation of the apparatus**

Immediately after polarization, the specimens were washed in water and then acetone, dried with a blast of cold air and introduced into the thoroughly outgassed hydrogen extraction apparatus by magnetic manipulation through the mercury reservoir 0 and column C. Occasionally a small air bubble was simultaneously introduced; this was removed from the system by the backing pump 2 with stop-cock T2 open. When the Pirani gauge registered a steady minimum reading again (this required approximately 30 s.) T2 was closed, the preheated furnace A withdrawn, the specimen manipulated into the hot zone of the silica furnace tube B, and the furnace replaced immediately. The specimen was then heated at the desired extraction temperature (usually 200°C) until the Pirani gauge
registered a steady (maximum) reading (this usually required about 45 minutes). The extracted gases (which usually consisted of 100% hydrogen) were then collected by the following procedure.

Stop-cock $T_1$, which was previously connected to the backing pump, was now opened to the atmosphere and air gradually admitted to the mercury reservoir, $F$, via the needle valve $N$. When the mercury level had risen beyond $T_3$, the reservoir $F$ was again evacuated through $T_1$, $T_3$ being closed simultaneously. This collection procedure was repeated several times until the Pirani gauge again registered the initial steady minimum reading (this usually required 5 - 6 collection operations). After the final collection, $T_1$ was left open to the atmosphere and the mercury level adjusted via needle valve $N$, to the desired calibrated volume mark. The head of mercury ($h_1$) in limb $M$ was now measured by means of a metre rule.

Now stop-cock $T_4$ was opened and the gases allowed to come into contact with the palladium tube pre-heated to 500°C. After 3 - 5 min, $T_4$ was closed and after re-adjusting the mercury level to the previous mark the head of mercury in limb $M$ was again measured ($h_2$).

The pressure of hydrogen in the system is given by $(h_1 - h_2)$ cm, mercury and conversion to N.T.P. will give the volume of hydrogen extracted from the specimen, e.g. 76
\[(H) = V \times \frac{h_1 - h_2}{P} \times \frac{273}{273 + T} \times \frac{100}{W}\]

where \(V\) = calibrated volume (ml.)

\(P\) = atmospheric pressure (cm. mercury)

\(T\) = atmospheric temperature

\(W\) = weight of sample (g).

This gives the hydrogen content in ml. hydrogen per 100 g steel. Conversion to p.p.m. hydrogen is relatively simple since 1 ml/100 g = 0.9 p.p.m.

After measurement the specimen, when sufficiently cooled, was withdrawn from the apparatus via the barometric mercury column.
4.1 Preliminary Experiments

In order to demonstrate the possibility of the type of delayed failure described in Section 2 (i.e. failure of high strength steel during sacrificial protection by anodic coatings), it was decided at the outset to carry out a limited number of delayed failure tests on cathodically polarized, notched cylindrical REX.539 test-pieces, using a Houndfield Tensometer at stresses below the notched tensile strength. A small perspex cell was therefore designed and constructed so that the test-piece could be cathodically polarized during delayed failure tests; a line diagram of the cell is shown in Fig.13. The cell was cylindrical in shape, with a cylindrical vertical tube to accommodate a standard reference electrode and an anode. Sealing the cell around the test-piece to prevent leakage of solution was achieved by the use of split P.T.F.E. sleeves coated with a proprietary stopping-off compound (Lacomit) and electrical connection to the test-piece (cathode) was made via one of the test-piece grips. A platinum anode was used, but no provision could be made for de-aeration of the solution during the experiment. Polarization was attained by means of a simple potentiostat (Shandon Ltd.), and the potential of the polarized test-piece was measured by means of a nylon Luggin capillary connected to a length of glass tubing, and hence to a 0.1 N calomel electrode via a Quickfit B14 cone and socket joint.
FIGURE 13

Detail of Cell

A - perspex cell

B - notched tensile steel specimen (cathode)

C - platinum anode

D - p.t.f.e. sleeves (split)

E - reference electrode assembly.
CELL FOR SIMULTANEOUS TENSILE STRESS / CATHODIC POLARIZATION STUDIES

FIGURE 13
The calomel electrode was supported fairly rigidly in a stand. When the test-piece fractured, one or both of the sleeves were pulled free and the cell remained intact. The solution escaped into a reservoir.

Because of the limited number of test-pieces available (owing chiefly to their high cost), it was decided (with one exception) to study delayed failure behaviour at one stress level only (i.e. 40% of the notched tensile strength), and at three different pH's (i.e. pH 4.0, 5.0 and 7.6). Solutions corresponding to the first two pH values were obtained by using acetic acid/sodium acetate mixtures, whilst the latter value was attained with potassium hydrogen phthalate. The results are shown in Table 4.
### TABLE 4
Results of simultaneous tensile stress/cathodic polarization experiments

<table>
<thead>
<tr>
<th>pH</th>
<th>mV</th>
<th>% N.T.S.</th>
<th>Additions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>40</td>
<td>None</td>
<td>no failure</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>40</td>
<td>&quot;</td>
<td>failed 15 min.</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>40</td>
<td>10 p.p.m. As</td>
<td>no failure</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>40</td>
<td>10 &quot; &quot;</td>
<td>failed 15 min.</td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>65</td>
<td>10 &quot; &quot;</td>
<td>failed 15 min.</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>40</td>
<td>None</td>
<td>no failure</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>40</td>
<td>&quot;</td>
<td>failed 15 min</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>40</td>
<td>10 p.p.m. As</td>
<td>no failure</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>40</td>
<td>10 &quot; &quot;</td>
<td>failed 15 min</td>
</tr>
<tr>
<td>7.6</td>
<td>0</td>
<td>40</td>
<td>None</td>
<td>no failure</td>
</tr>
<tr>
<td>7.6</td>
<td>100</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>7.6</td>
<td>200</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>7.6</td>
<td>400</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>7.6</td>
<td>450</td>
<td>40</td>
<td>&quot;</td>
<td>no failure</td>
</tr>
<tr>
<td>7.6</td>
<td>300</td>
<td>40</td>
<td>10 p.p.m. As</td>
<td>failed 15 min.</td>
</tr>
</tbody>
</table>
These results exhibit several striking features. Firstly, at the relatively low stress level used, failure was induced very rapidly during cathodic polarization at 100 mV over-voltage in solutions of pH 4 and 5. Since the test-pieces revealed no visible signs of corrosion, failure could reasonably be attributed to lowering of the notched tensile strength by absorbed hydrogen. Secondly, at pH 7.6, delayed failure did not occur within the times investigated (i.e. 8 h) until the overvoltage exceeded 450 mV (about 300 mV in the presence of 10 p.p.m. arsenic), when rapid failure again occurred. Thirdly, when small amounts of arsenic were added to the electrolyte solution failure occurred at pH 4 and 5, and at applied tensile stresses equivalent to 40% of the notched tensile strength only when the overvoltage exceeded 300 mV. Delayed failure was caused, however, at 250 mV over-voltage when stress level was raised to 60% of the notched tensile strength. A possible explanation for this apparent 'inhibitive' action of arsenic within this narrow range of pH, overvoltage and applied tensile stress is offered later. Fourthly, whenever delayed failure occurred, the incubation time to failure was always very nearly constant (i.e. approximately 15 min.), which suggested that the same process (i.e. migration of hydrogen to some critical region of the test-piece, possibly the triaxial stress concentration
at the base of the notch) was responsible for failure in all cases.

It is submitted that these experiments, which were simple in outline and which were carried out before hydrogen analysis facilities were available, demonstrated the possibility of delayed failure in high strength steels under conditions simulating protection by anodic coatings at pores and discontinuities in the coating.

4.2 Influence of Extraction Temperature on Hydrogen Estimation

This section describes the work carried out to ascertain the most suitable temperature for hydrogen extraction. This was considered necessary as there was a considerably diversity of opinion on this point. Actual temperatures employed by previous workers have varied from 250°C to 1050°C, although the most commonly used temperature (at least for ferritic steels) appears to be 600 - 650°C; Sloman \(^{102}\) and Newell \(^{103}\) have stated, for instance, that evolution of hydrogen is complete in 0.5 - 1 h. at this temperature. There is some doubt as to whether this is the case, however, and a group of French workers \(^{112}\) have suggested that hydrogen evolution at temperatures of 600°C and below occurs in two stages. During the first stage (of approximately 1 h. duration) they found that only 75 - 80% of the hydrogen was evolved from unalloyed steels; the remainder was then extracted only very slowly over a period of 2 - 3 days.
Darken and Smith\textsuperscript{61} employed the relatively low temperature of 200 - 280°C to extract hydrogen absorbed by steel during immersion in acid solutions. They claimed that evolution of this mobile form of hydrogen at this temperature was complete in approximately 1 h.

In order to ascertain the most suitable extraction temperature for the present work, gas evolution experiments were performed in the hydrogen estimation apparatus (Figs. 8 - 12) at temperatures in the range 200 - 700°C using REX.539 steel rod, both in the as-received condition and after cathodic polarization in 0.5 M sulphuric acid. It was anticipated that any hydrogen extracted from the as-received steel would be 'residual' (molecular) hydrogen, and that hydrogen extracted after polarization would consist of both 'diffusible' and 'residual' hydrogen. The different forms in which hydrogen is thought to be capable of existing in steel are discussed later. (Section 5).

Fig. 14 shows the amounts of hydrogen (expressed in p.p.m. in the steel) evolved from REX.539, in the as-received condition at temperatures of 200 - 700°C during periods of up to 7 h. Several points from this figure merit attention. First, scarcely any hydrogen was evolved at 200°C (only 0.02 p.p.m. in 7 h.), and the amount evolved at 400°C was not much greater than this.
Hydrogen evolution/time curves for as-received REX.539 heated in vacuum

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
</tr>
</tbody>
</table>
Secondly, an appreciably fast rate of evolution occurred during the initial 30 min. extraction at 500°C and above. Thirdly, after approximately 1½ h. a slower linear evolution rate was achieved at all temperatures studied. This constant secondary rate increased with increase in extraction temperature.

At first sight it seemed apparent that these results did not support Sloman's and Newell's contention that vacuum extraction of hydrogen from steel is complete in approximately 1 h. at 600°C. The slow linear secondary rate did not, however, appear to suggest evolution of 'real' hydrogen from the steel, although this could correspond to the second stage of hydrogen evolution described by J. Bleton et al. However, an alternative explanation was considered. It had previously been shown by Brittain that evolution of hydrogen from steel at elevated temperatures is accompanied by a reaction between the steel specimen and water vapour (which is presumably adsorbed on the surface of the specimen and is thus carried into the vacuum apparatus). Reaction could be simply between the iron and water vapour resulting in oxidation of the iron, or alternatively the water vapour could react with carbon in the steel, giving carbon monoxide and hydrogen. If the latter reaction occurred, small amounts of gas other than hydrogen (i.e. carbon monoxide) would be produced; it was indeed noticed that small amounts of an unidentified gas were evolved at temperatures
in excess of 300°C. In order to explore this possibility still further, an additional series of vacuum extraction experiments were performed on REX.539 steel which had previously been heated in vacuum at 700°C. for 24 h. to remove 'residual' hydrogen as completely as possible and then exposed to the atmosphere by withdrawal through the mercury column C (Fig.10). The results are shown in Fig.15. The form of these curves, with the exception of the pattern of evolution in the first hour, is markedly similar to those in Fig.14; thus, after the first hour, a linear evolution rate is again attained at all temperatures between 200 and 700°C, and this rate is again temperature-dependent. Again, small amounts of a gas other than hydrogen were evolved at temperatures greater than 300°C.

These results would seem to confirm the hypothesis that adsorbed water reacts with the steel specimen at elevated temperatures and thus interferes with results obtained for the hydrogen content of steel by vacuum extraction. This was indicated yet again by holding a pad soaked in liquid air over the top of the mercury column during introduction and heating of the specimen, when the rate of hydrogen evolution from as-received REX.539 was markedly lowered, particularly at the higher temperatures.
FIGURE 15

Hydrogen evolution/time curves for REX.539 heated in vacuum after previous vacuum heat-treatment (5 h at 700°C followed by exposure to atmosphere)

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
</tr>
</tbody>
</table>
Having established that hydrogen estimation by vacuum extraction at temperatures greater than 300°C could lead to uncertain results, deliberate introduction of hydrogen into REX.539 was carried out by cathodically charging annealed specimens 1 in. x 0.2 in. dia. at a current density of 0.25 mA/cm² in 0.5 M sulphuric acid. Vacuum extraction was then carried out on the charged specimens over the temperature range 200 - 700°C; the results are presented in Fig.16.

The most important observation from these results is that appreciable quantities of hydrogen (presumably the 'diffusible' variety) were evolved at 200°C. In fact during the first hour of extraction the amount of hydrogen evolved at 600°C and 700°C was little greater than that evolved at 200°C. After the first hour, a slow linear evolution rate was again clearly noticeable at temperatures between 300 and 700°C; only a very small amount of hydrogen, however, (0.02 p.p.m. in 5 h.) was evolved at 200°C. The linear secondary evolution rate at 600°C and 700°C was almost identical to that measured from as-received REX.539.

It is significant that in the early stages of extraction, evolution at 200°C is almost as fast as the rate at 700°C. Furthermore on raising the temperature to 700°C after extraction for 1 h. at 200°C, an evolution curve similar to curve 1 (Fig.15)
FIGURE 16

Hydrogen evolution/time curves for REX.539 heated in vacuum after cathodic polarization at a current density of 0.25 mA/cm² for 1 h. in 0.5 M sulphuric acid.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
</tr>
</tbody>
</table>
was obtained. It would therefore appear that 'diffusible' hydrogen at least, can be extracted from cathodically polarized REX.539 fairly rapidly (i.e. within 45 - 60 min.) at 200°C, provided that extraction is carried out immediately following polarization. Since the water reactions appears to be almost insignificant at this temperature, and furthermore since it is now widely accepted that 'diffusible' (and not 'residual') hydrogen is responsible for embrittlement, there is clearly a strong case for determining hydrogen absorbed during cathodic polarization, pickling, or electroplating, by vacuum extraction at 200°C. Certainly for the present purpose high-temperature extraction seemed neither desirable nor necessary, and results obtained at 200°C appeared to be far more significant and reliable. Consequently low-temperature extraction was adopted for the present work.

4.3 Factors Influencing Hydrogen Absorption by REX.539 during Cathodic Polarization.

4.3.1 Experimental

Cathodic polarization experiments followed immediately by hydrogen analysis were carried out by potentiostatic and galvanostatic techniques on REX.539 rod over a wide range of experimental conditions using the techniques described in Sections 3.1, 3.2, 3.3 and 4.2. In order to provide a datum line for these experi-
ments it was decided to select an arbitrary 'standard' set of conditions for polarization experiments. The 'standard' conditions chosen were as follows:

1. REX.539 steel, oil-quenched from 865°C and tempered at 600°C (1 h.);
2. Solution: sodium acetate/acetic acid buffer (pH 4.0);
3. Overvoltage of cathode 100 mV (for potentiostatic experiments);
4. Duration of polarization 3 h.

An experiment performed under these conditions was found to result in the absorption of 0.12 p.p.m. hydrogen by the steel (see Fig.17(a)). The 'standard' conditions were subsequently used as a means of checking different batches of REX.539 for reproducibility. Each of these conditions was then varied independently so that the effect of each factor on absorption of hydrogen could be determined. Eventually a complex pattern of results covering all factors was obtained.
4.3.2 Dependence of hydrogen absorption on duration of polarization

Graphs showing the relationships obtained between hydrogen absorbed and polarization time for a variety of experimental conditions are shown in Figs.17(a) to (d). The results for a solution pH of 4.0 (Figs.17(a) to (c)) are arranged in three groups of three graphs each; each group represents a particular overvoltage, each curve in each group refers to a given steel tempering temperature. Thus Figs.17 to 19 in reality represent the effect of three variables (i.e. duration of polarization, overvoltage and metallurgical condition as influenced by tempering temperature) on hydrogen absorption of 316L539, with only solution pH and impurity level remaining constant throughout. The influence of solution pH on hydrogen absorption/polarization time curves is illustrated in Fig.17(d) for 'standard' conditions of overvoltage (i.e. 100 mV) and steel tempering temperature (i.e. 600°C).

A general feature of all hydrogen absorption/polarization time curves presented here is that they show an initially linear relationship between hydrogen absorbed and duration of polarization (stage 1). At longer times, the curves gradually transform to an approximately horizontal portion (stage 2). The time for the occurrence of transition from stage 1 to stage 2 appears to be independent of pH (Fig.17(d)), but varies with the tempering
Dependence of amount of hydrogen absorbed by REX.539 on duration of cathodic polarization (potentiostatic technique).

(a) Acetate buffer pH 4.0; overvoltage 100 mV

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>

(b) Acetate buffer pH 4.0; overvoltage 150 mV

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>600</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>6</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>

(c) Acetate buffer pH 4.0; overvoltage 200 mV

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
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</thead>
<tbody>
<tr>
<td>7</td>
<td>600</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
</tr>
<tr>
<td>9</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>

(d) Tempering temperature 600°C; overvoltage 100 mV

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>acetate buffer pH 5.0</td>
</tr>
<tr>
<td>11</td>
<td>&quot;             pH 5.5</td>
</tr>
<tr>
<td>12</td>
<td>&quot;             pH 6.0</td>
</tr>
</tbody>
</table>
POLARIZATION TIME, h

HYDROGEN ABSORBED, ppm

(a)
(b)

HYDROGEN ABSORBED, ppm

Polarization Time, h
HYDROGEN ABSORBED, ppm

POLARIZATION TIME, h

(d)
temperature (i.e., with the metallurgical condition) of the steel. In general, the higher the tempering temperature, the more prolonged is the transition time. For instance, the transition occurs at 8 - 10 h. for REX.539 tempered at 600°C (curves 1, 4, 7), at 5 - 6 h. for the same steel tempered at 400°C (curves 2, 5, 8), and at 3 - 4 h. for untempered or lightly tempered (i.e., 200°C) REX.539 (curves 3, 6, 9). (Figs. 17(a), (b), (c) respectively).

The horizontal portion of each curve (i.e., stage 2) probably represents the 'saturation concentration', $C_s$, of hydrogen in REX.539 for each given set of experimental conditions. It is noticeable that there is a greater degree of scatter in the results in this region; this is in accordance with previous work. The scatter in some cases (i.e., curve 1, Fig. 17(a), 16 h.) is so pronounced as to suggest 'supersaturation'. This has also been observed by Schuetz and Robertson.

4.3.3 Dependence of hydrogen absorption on overvoltage

From examination of Figs. 17(a) to (c) it is apparent that at a solution pH of 4.0, an increase in overvoltage results in increased absorption of hydrogen by REX.539. In order to show this more clearly, some of the results in Figs. 17(a) to (c), together with some additional data for intermediate overvoltages, have been re-plotted in the form of hydrogen absorption/applied
overvoltage curves. The results are shown in Figs.18(a) and (b). Fig.18(a) refers to hydrogen absorption of REX.539 (in a variety of metallurgical conditions) under standard conditions of solution pH (i.e. 4.0) and duration of polarization (i.e. 3 h.) Fig.18(b) represents hydrogen absorption versus overvoltage for conditions of hydrogen 'saturation' (i.e. for polarization times longer than 15 h.). In all cases it is evident that for overvoltages between 50 and 200 mV, hydrogen absorption of REX.539, both in the untempered or lightly tempered condition (curve 3, Figs.18(a) and (b)), and when fully tempered (curve 1, Figs.18(a) and (b)), is directly proportional to overvoltage, provided other conditions are constant. Absorbed hydrogen does not appear to be readily detected in REX.539 polarized at overvoltages less than 25 - 30 mV in a solution of pH 4.0, irrespective of tempering temperature.

The effect of increasing solution pH on the hydrogen absorption/overvoltage relationship is shown in Fig.19. Curves 1 and 3 depict the relationship for REX.539 tempered at 600°C and 200°C respectively, both at a solution pH of 5.0; curves 2 and 4 are again representative of REX.539 tempered at 600°C and 200°C respectively, this time at pH 5.5. It can be seen that whereas the linear relationship between absorbed hydrogen and overvoltage is still obeyed at pH 5.0, there is a marked deviation from linearity at pH 5.5.
FIGURE 18

Dependence on amount of hydrogen absorbed by REX.539 on overvoltage (potentiostatic technique).

(a) Acetate buffer pH 4.0; duration of polarization 3 h

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>

(b) Acetate buffer pH 4.0; duration of polarization 15 h (i.e. saturation)

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>
FIGURE 19

Dependence of amount of hydrogen absorbed by REX,539 on overvoltage (potentiostatic technique). Duration of polarization 3h.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetate buffer pH 5.0; tempering temperature 600°C.</td>
</tr>
<tr>
<td>2</td>
<td>pH 5.5; 600°C.</td>
</tr>
<tr>
<td>3</td>
<td>pH 5.0; 200°C.</td>
</tr>
<tr>
<td>4</td>
<td>pH 5.5; 200°C.</td>
</tr>
</tbody>
</table>
The results described were obtained using careful experimental conditions, an essential feature being de-oxygenation of solutions both before and during polarization, as described in Section 3.2.3. When similar experiments were performed on REX.539 at pH 4.0 with the de-oxygenation stage omitted, the relationship obtained between absorbed hydrogen and overvoltage (curve 1, Fig.20) was non-linear, particularly at overvoltages greater than 100 mV. This was also the case at pH 5.5 (curve 2, Fig.20), although at this pH deviation from linearity was noticeable even when de-oxygenation was carried out.

The importance of pH control of the electrolyte solution is made clear by the results (Fig.21) of potentiostatic polarization experiments performed with 0.5 M sodium sulphate (pH 5). The deviation from linearity is marked, and the amount of hydrogen absorbed under all conditions is less than that absorbed during polarization in buffered solutions of the same pH.

4.3.4 Dependence of hydrogen absorption on metallurgical structure of steel.

In order to study the effect of differences in metallurgical structure on hydrogen absorption, polarization experiments were carried out potentiostatically on REX.539 quenched and tempered at various temperatures. This enabled structures ranging from martensite to sorbite (a fine agglomeration of spheroidal iron carbide in a matrix of ferrite) to be studied. As can be seen
Dependence of amount of hydrogen absorbed by REX.539 on overvoltage (potentiostatic technique).

Acetate buffer (no de-oxygenation);
duration of polarization - 3 h;
tempering temperature - 600°C.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
</tr>
</tbody>
</table>
FIGURE 21

Dependence of amount of hydrogen absorbed by REX.539 on overvoltage (potentiostatic technique).

Unbuffered 0.5 M sodium sulphate (pH approximately 5.0);

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>
from Figs. 17(a) to (c), and again from Figs. 18(a) and (b), the various structures show marked differences in hydrogen-absorbing capacity. REX.539 tempered at 600°C shows the highest rate of hydrogen absorption, whilst untempered or very lightly tempered material (i.e. tempered at 200°C) appears to absorb only small amounts of hydrogen. The behaviour of partly tempered REX.539 (i.e. tempered at 400°C) is intermediate between these two extremes. Pure iron, however, was found to absorb even less hydrogen than untempered REX.539; even when polarization was carried out at an overvoltage of 400 mV at pH 4.0 in an acetate buffer solution for 24 h., only about 0.04 p.p.m. hydrogen was found in the iron by vacuum extraction at 200°C.

As has already been pointed out in Section 3.2.3, hydrogen 'saturation' conditions appeared to be attained much faster in untempered REX.539 than in the same material tempered at 600°C.

4.3.5 Dependence of hydrogen absorption on impurities in the electrolyte.

In view of the puzzling results obtained in preliminary delayed failure experiments, when arsenic was found to have an inhibitive action on embrittlement resulting from cathodic polarization in solutions of pH 4 to 5 within a narrow range of overvoltage and applied stress, it was decided to make a more detailed study.
of the effect of small additions of arsenic to the electrolyte on hydrogen absorption by REX.539 during potentiostatic cathodic polarization. In addition, $\eta/i$ and $\gamma/log i$ curves were plotted for galvanostatic conditions. The requisite amount of arsenious trioxide dissolved in sodium hydroxide was added to solutions to give arsenic concentrations of 1, 5 and 10 p.p.m. In view of the small quantities added, no change in pH resulted.

The results for hydrogen absorption during potentiostatic experiments are shown in Table 5; 'standard' conditions of polarization duration, solution pH and steel metallurgical condition (see Section 4.3.1) were employed for all experiments.

From these results it can be seen that whereas at 100 and 200 mV overvoltage, hydrogen absorption decreased when arsenic was present in solution, the reverse behaviour occurred at 300 mV overvoltage, when hydrogen absorption increased with increasing arsenic concentration. The increase, however, was not of the magnitude expected. Furthermore, the decrease in hydrogen absorbed by REX.539 at 100 and 200 mV overvoltage due to arsenic was virtually independent of arsenic concentration. The implication from this evidence is that a very thin (perhaps monomolecular) layer of some arsenical species deposited in the cathode is responsible for partial inhibition of hydrogen absorption.
TABLE 5

Hydrogen absorbed by REX.539 during cathodic polarization in arsenic-containing buffered acetate solutions (pH 4.0) (REX.539 tempered at 600°C; duration of polarization 3 h)

<table>
<thead>
<tr>
<th>Overvoltage, mV</th>
<th>As concentration, ppm</th>
<th>Hydrogen absorbed, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0.12</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>0.07</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0.40</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>0.20</td>
</tr>
<tr>
<td>200</td>
<td>5</td>
<td>0.17</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>0.16</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0.70</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>1.04</td>
</tr>
<tr>
<td>300</td>
<td>5</td>
<td>1.10</td>
</tr>
<tr>
<td>300</td>
<td>10</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Figs. 22(a) and (b) shows the $\eta/i$ and $\eta/\log i$ curves obtained by galvanostatic cathodic polarization of REX.539 with 1, 5 and 10 p.p.m. arsenic present in the electrolyte. The influence of arsenic in raising the overpotential for hydrogen evolution is clear from these results.
FIGURE 22

Overvoltage/current density curves (22(a)) and Tafel plots (22(b)) for REX. 539 (tempered at 600°C.), cathodically polarized in acetate buffer (pH 4.0) with arsenic added.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Arsenic Added, p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>

110—111
The present work represents a study of some of the factors which affect the rate of hydrogen absorption during cathodic polarization of a typical high-strength steel in an aqueous solution. The experimental conditions chosen have been based to some extent on the conditions which could prevail at a steel surface which is partly coated with a more electronegative metal; it has been established, for example, that coupling REX.539 with cadmium in neutral 3% sodium chloride results in depression of the steady-state potential of the steel by approximately 50 mV.

Although near-neutral solutions are more significant for service conditions than the strongly acid solutions used for deliberate charging of steel with hydrogen, they have the disadvantage that pH changes occur at the cathode during evolution of hydrogen; for this reason sodium acetate/acetic acid buffers rather than neutral chloride solutions were selected for these studies.

In the present study, potentiostatic conditions have been used in the majority of experiments as it is considered that they represent a more fundamental approach to the problem. In galvanostatic studies the true current density requires a knowledge of the true surface area which in turn depends upon surface preparation, and it is far simpler in practice to measure a potential rather than a galvanic corrosion current.
The experimental conditions of charging have been rigidly controlled, and attention has been paid to solution purity, with particular emphasis on exclusion of oxygen. Under the conditions described it has been shown that introduction of hydrogen into a high tensile steel during potentiostatic cathodic polarization is highly reproducible, and that hydrogen introduced in this way can be completely removed from the steel in vacuo, at temperatures as low as 200°C. High extraction temperatures have been shown to be undesirable owing to possible errors which may arise due to reaction of adsorbed water vapour with the steel - a possibility which cannot be discounted under most experimental conditions of hydrogen determination.

Parallel studies of the effect of absorbed hydrogen on mechanical properties (in particular, delayed failure) have not been made owing to the necessity of performing a large number of experiments on accurately machined, notched tensile test-pieces. It has been demonstrated, however, that delayed failure of high strength steels can occur under conditions simulating protection by anodic metal coatings at pores and discontinuities in the coating, particularly when the pH of moisture droplets adhering to the metal surface falls below about pH 5, and probably also in the presence of small amounts of atmospheric impurities (hydrogen sulphide, for instance) which act as 'poisons' for the cathodic hydrogen evolution reaction and favour entry of hydrogen into the metal.
It is well known that the hydrogen evolution reaction occurs by a series of well-defined stages and that, depending on the particular system, any one (or more) of these steps may be rate-determining. The steps for evolution from strong acid solutions were mentioned briefly in Section 2. The Tafel equation is applicable when the rate of the reverse reaction (ionization of hydrogen gas) can be neglected; i.e. when the overvoltage is greater than 50 mV, and under these conditions

\[ \eta = a + b \log i \]

where \( a \) and \( b \), the Tafel parameters, may be diagnostic of the rate-determining step. A review of Tafel parameters in relation to the mechanism of hydrogen evolution has been given by Barton.\(^{44}\)

It is evident that any discussion of the entry of hydrogen into metals must involve a consideration of the mechanism of the hydrogen evolution reaction of the particular system. Nernst\(^ {114}\) pointed out that highly occluding metals have comparatively low values of hydrogen overvoltage (e.g. platinum, palladium, iron, copper, nickel), whilst metals which are either slightly occluding or non-occluding with respect to hydrogen have larger \( \eta \) values (e.g. mercury, lead, zinc, cadmium). At least one metal, gold, by virtue of a relatively low value of \( \eta \) combined with a very small occlusive capacity, proved an exception to this rule, and this led Smith\(^ {115}\) to suggest that velocity rather than capacity for occlusion
is the prime consideration. Smialowski\textsuperscript{116} considers that in addition to the usual processes comprising hydrogen evolution, an additional process should be taken into account for metals which possess a high occlusive capacity for hydrogen; i.e.

\[ X \text{HADS} + M \rightarrow \text{MHX} \]

He argues that since penetration of hydrogen into the cathode provides an alternative means of escape for hydrogen from the surface, then the energy of the metal phase may be changed due to occluded hydrogen, and hence \( \gamma \) may be affected.

From the point of view of the present study it should be pointed out that previous \( \eta/i \) studies have in general been confined to strongly acid or strongly alkaline solutions. The reason for this is not surprising, since in the neutral region, pH changes at the metal/solution interface with the consequent possibility of alternative reactions may complicate the interpretation of results. Thus, Bockris\textsuperscript{91} has shown that simultaneous reduction of both \((H_3O)^+\) and \(H_2O\) is energetically possible at pH 7 - 8, so that reduction of both species to hydrogen occurs simultaneously.

Furthermore, it should be observed that the nature of the cathode surface is of the greatest significance in the mechanism of the hydrogen evolution reaction; in view of this is is unlikely that Tafel parameters for pure iron are applicable to the martens-
sitic and sorbitic structures of the steels used in the present work. This was confirmed by constant current polarization experiments (Fig. 23). The side reaction of hydrogen absorption for pure iron and tempered (sorbitic) high-strength steel also seems to differ since, under the conditions used in the present study, little hydrogen enters pure iron during cathodic polarization, whereas appreciable quantities are absorbed by REX539 tempered at 600°C.

In considering the various rate-determining steps for hydrogen evolution, diffusion of hydrogen ions to the cathode can be disregarded in the present study, since low currents and turbulent conditions were employed. Furthermore, the concentration of hydrogen molecules adsorbed on the surface of a cathode is considered to be negligible for all mechanisms, with the exception of hydrogen discharge on highly activated platinum.

The hydrogen entry side-reaction can now be analysed in relation to the present work. As was mentioned in Section 2, the various stages comprising this process are as follows:

1. adsorption of hydrogen atoms on the metal surface,
2. transfer of adsorbed atoms from the surface into the metal lattice (i.e. solution in the metal),
3. diffusion of dissolved atoms (or protons) within the metal phase.
FIGURE 23

Tafel plots for REX.539 tempered at varying temperatures, and for pure iron.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C</th>
<th>Tafel Constant &quot;b&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>pure iron</td>
<td>0.095</td>
</tr>
</tbody>
</table>
For the present purpose, the stages involved in desorption of hydrogen from the metal will not be considered.

It is not clear whether hydrogen which enters steel during cathodic polarization is in the form of dehydrated protons or uncharged atoms. Baukloh and Zimmerman observed a maximum flow of hydrogen through steel membranes cathodically polarized in sulphuric acid at a concentration of 10 N, which corresponds approximately to the maximum hydrogen ion activity. Darmois has suggested that passage of hydrogen through steel occurs at least partly in the form of protons. If this is the case, then it would be expected that cathodic polarization in strong acid solutions would certainly lead to absorption of protons by the steel, since hydrogen evolution occurs from this source. In neutral solutions, however, evolution of hydrogen results largely from reduction of water molecules, and thus the main species entering steel in this medium would presumably by atomic hydrogen.

It is apparent that hydrogen can exist in several forms within steel. Firstly, it can enter into interstitial solution in the iron lattice as hydrogen atoms or protons. Secondly, it can be trapped in defects, either in the atomic state (in dislocations and vacant lattice sites) or in the molecular state (in larger voids). The combined form of hydrogen within the metal is generally regarded as non-diffusible and harmless, whereas the diffusible form is generally regarded as responsible for embrittlement and delayed failure. This is discussed in more detail later.
It has been suggested that the rate of absorption of protons or hydrogen atoms by an iron cathode during polarization will be dependent on the rate of diffusion of hydrogen (irrespective of form) within the electrode material. Thus Darken and Smith have shown that the concentration of hydrogen absorbed by mild steel during immersion in acid for periods of time shorter than that required for saturation is proportional to the square root of exposure time. Similarly, Schuetz and Robertson have established a linear relationship between absorbed hydrogen and $\sqrt{\text{time}}$ for Armco iron cathodically charged in sulphuric acid or in an aqueous solution of hydrogen sulphide. As shown by Darken and Gurry, this is in agreement with accepted principles of diffusion as defined by Fick's Laws.

The initial linear absorption rate observed in the present work suggests, however, that diffusion is not the rate-controlling process in permeation of hydrogen into steel during cathodic polarization in near-neutral solutions. The question then arises as to which of the other two processes, i.e. adsorption or solution, is rate-controlling. There is some evidence that under certain conditions hydrogen does not enter into true interstitial solution in the iron lattice at temperatures below about 130°C. Hewitt, for instance, measured the internal friction of a high tensile steel charged with hydrogen, at elevated temperature and showed that no internal friction peak existed.
He suggested that hydrogen became trapped in voids (possibly dislocations) at temperatures below 130°C. Internal friction peaks were obtained, however, with specimens which had been cathodically charged with hydrogen in a 'poisoned' acid solution. In this case it was considered that extremely high pressures of hydrogen (of the order of $10^7$ atm.) were developed within lattice defects in the steel, and this resulted in hydrogen passing into interstitial solution in the iron lattice in accordance with Sieverts' Law. Furthermore, the observations of Hobson and Barancwski concerning anomalies in the diffusion coefficient of hydrogen in steel at ambient temperatures (see Section 2) suggest that at these temperatures there is some limitation in the interstitial solubility of hydrogen in steel. If this is the case, then solution in the metal may well be the rate-controlling factor in absorption of hydrogen by REX.539 during cathodic polarization in near-neutral solutions.

On the other hand, it could equally well be argued that coverage of the cathode surface with adsorbed hydrogen may not be complete under these conditions.
Low coverage of the cathode surface, however, is indicative of a rate-determining slow discharge mechanism. Since the 'b' value for both rate-determining slow discharge and electrochemical desorption mechanisms are very similar, (0.122 for hydrogen evolution on iron in strong acid solutions, according to Pentland et al), then it is impossible to distinguish between these two mechanisms by this means. If it is assumed that the rate of hydrogen entry is linear with time and is governed by low coverage of the cathode surface with adsorbed hydrogen, then a linear absorption rate may be diagnostic of a rate-determining slow discharge mechanism of hydrogen evolution. It follows from this line of reasoning that a hydrogen absorption rate proportional to \( \sqrt{\text{time}} \) with a high coverage of the cathode surface, as was observed by Schuetz and Robertson for hydrogen absorption by Armco iron during cathodic charging in strong acid solutions, would be indicative of a rate-controlling electrochemical desorption mechanism. The relationship obtained by Schuetz and Robertson was confirmed on REX.539 (hardened and tempered at 600°C) by cathodic polarization in 0.5 M sulphuric acid, when a linear hydrogen absorbed vs. \( \sqrt{\text{time}} \) relationship was obtained. The results of this experiment are shown in Fig.24. Thus, if the foregoing interpretation of the present results is correct, the mechanism of hydrogen evolution on steel in solutions of intermediate pH (4.0 to 5.5) differs from that operative in strong acid solutions.
FIGURE 24

Hydrogen absorption/square root time curve for hydrogen absorption by REX.539 tempered at 600°C. and potentiostatically polarized in 0.5 M sulphuric acid (overvoltage 100 mV)
A linear relationship between overvoltage, \( \eta \), and absorbed hydrogen has been consistently observed in the present work for hydrogen absorbed by REX.539 steel during cathodic polarization in solutions of pH 4 - 5 and at overvoltages between 50 - 200 mV. Since the Tafel equation for hydrogen evolution is only operative when \( \eta \) is greater than 50 mV, and since negligible amounts of hydrogen are absorbed by REX.539 when \( \eta \) is less than 50 mV, then it is clear that hydrogen absorbed during polarization is directly connected with some stage of the hydrogen evolution reaction. These results are in agreement with those of Schuetz and Robertson, who observed that for hydrogen absorption by Armco iron from acid solutions the saturation concentration (cₐ) of hydrogen is related to the current density by an equation similar to the Tafel relationship:

\[
[H]_{ABS.} = a + b \log i
\]

This linear relationship between \([H]_{ABS.}\) and \(\log i\) was confirmed in the present work by galvanostatic cathodic polarization of REX.539 steel, and the results are shown in Fig. 25. Since

\[
\eta = a + b \log i
\]

for hydrogen evolution, then \(\eta\) should be directly proportional to \([H]_{ABS.}\), as was observed in the present work. At higher pH values, however, this relationship is not obeyed, and the results
**FIGURE 25**

Hydrogen absorption/log. current density curves for hydrogen absorbed during galvanostatic cathodic polarization of REX.539 in acetate buffer (pH 4.0).

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Tempering Temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200 (and untempered)</td>
</tr>
</tbody>
</table>
show that at pH 5.5 and above, $[H]_{ABS}$, is no longer proportional to $\eta$. This again is consistent with hydrogen evolution characteristics, since the hydrogen ion concentration is now decreasing and discharge of hydrogen will occur to an increasing extent from H$_2$O molecules. The change in the mechanism of hydrogen evolution on increasing the solution pH above 6.0 is emphasized by the results for hydrogen absorption by REX.539 during cathodic polarization in unbuffered 0.5 M sodium sulphate solution (pH 5.0), the results of which are presented in Fig.21. The deviation from linearity of the hydrogen absorbed/overvoltage relationship is probably due to a rise in pH in the vicinity of the steel cathode, with a resultant decrease in the amount of hydrogen entering the steel.

Cathodic polarization of REX.539 in solutions having a pH greater than 7.0 (e.g. sodium borate/boric acid solutions buffered to pH 8 - 10), led to even smaller amounts of hydrogen being absorbed by the steel than with neutral solutions. The results of these experiments are shown in Fig.26. From the more practical viewpoint, the decrease in hydrogen absorbed with increase in pH may explain why embrittlement due to hydrogen is rarely encountered during cathodic protection of steel structures. Reports of failure under such conditions are rare, one of the few known being that of Bruckner and Myles. Both formation of alkali at the cathode and depolarization by oxygen will combine to prevent hydrogen from entering the metal.
Hydrogen absorption/overvoltage curves for hydrogen absorbed by REX.539 (tempered at 600°C) during potentiostatic cathodic polarization in buffered sodium borate/boric acid solutions.

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
</tr>
</tbody>
</table>
A significant fact which emerged from the present work was the relative ease with which reproducibility of hydrogen absorption results was attained in potentiostatic experiments compared with the difficulty experienced with galvanostatic experiments in this respect. This suggests that although the amount of hydrogen discharged in a cathodic reaction depends on the charge, \( q \), the amount absorbed by the cathode material is more closely dependent on the value of the overvoltage, \( \gamma \).

From the results of Figs.17(a) to (c) and Figs.18(a) and (b), described in Section 4, it would seem that metallurgical structure plays an important part in the ability of REX.539 to absorb hydrogen during cathodic polarization. The results show that tempering at 600°C to give a very fine precipitate of Fe\(_3\)C results in much greater hydrogen absorption rates compared with untempered or lightly tempered REX.539. This is surprising at first sight, since it is generally accepted that structures containing martensite show a much greater susceptibility to delayed failure than structures produced as a result of hardening and tempering. It is also surprising that saturation with hydrogen appears to be achieved much more rapidly (4 h.) in martensitic REX.539 than in the same material having a sorbitic structure (15 h.).

Before further discussion of these observations, it is necessary to review the various mechanisms that have been postulated to explain the effect of hydrogen on the mechanical properties of iron and steel, particularly the following observations:
1. Hydrogen has no effect on the elastic properties or hardness.

2. The fracture stress is lowered in proportion to the hydrogen concentration, and the resulting fracture is essentially a brittle one.

3. Hydrogen can produce a small yield point in pure iron at low temperature. At normal temperatures, hydrogen has been reported to suppress the occurrence of the normal yield-point in mild steel.

4. Elongation and reduction in area are lowered in proportion to the hydrogen content.

5. Embrittlement is reduced with increasing strain rate, providing that the temperature is not below about -100°C and not above approximately 100°C.

6. Hydrogen embrittlement appears to require the presence of tensile stresses and also diffusible hydrogen for its initiation.

7. The phenomenon of delayed failure of high strength steels due to trace amounts of hydrogen must be accounted for.

Early theories proposed that the lowering of ductility was due to a strain-hardening effect caused by an Fe/H compound.
As has already been pointed out, however, iron does not appear to form a hydride. Later, Zapffe put forward the 'planar pressure' theory based on a simple ageing phenomenon in which the precipitate is hydrogen gas. He suggested that atomic hydrogen diffusing in the lattice was discharged into lattice 'rifts' forming molecular hydrogen and creating very high pressures capable of initiating fracture when the metal is subsequently strained. This theory does not account for the strain-rate and temperature-dependence of hydrogen embrittlement found by Brown, nor does it explain the continuous decrease in ductility observed with increasing hydrogen content.

Kazinczy proposed a modification to Zapffe's theory which accounts for the latter. He suggested that the lattice 'rifts' described by Zapffe are essentially Griffith cracks. Initially the rate of crack growth will be slow because diffusion of hydrogen to the crack is necessary. When hydrogen has precipitated in the crack, however, and an equilibrium pressure has been established, the resulting extension of the crack results in adiabatic expansion of the gas and additional energy is released. Thus, less strain energy is required to counterbalance the energy needed to form a new crack surface. The higher the hydrogen content of the metal, the greater is the resulting hydrogen pressure inside the crack and hence a lower applied stress will be sufficient for crack propagation.
Kazinczy's theory satisfactorily accounts for the strain-rate dependence of embrittlement, and its decrease below room temperature. It does not, however, explain why embrittlement decreases with increase in temperature above room temperature.

Petch, in moving a stage further than Zapffe, related hydrogen embrittlement to the Griffith mechanism of brittle fracture. He proposed that atomic (and not molecular) hydrogen was adsorbed on the surface of micro-cracks, lowering the strain energy required to form a new surface and thus permitting crack extension at lower applied stresses. Again, Petch's theory does not account for the disappearance of embrittlement above 100°C.

Bastien and Azou, and later Vaughan and de Morton, put forward a theory based on interaction of hydrogen and dislocations. Basically, they suggest that hydrogen atoms, which are initially present throughout the lattice, migrate under the influence of strain to active slip planes and form 'atmospheres' which hinder dislocation movement and lead to premature fracture. This is essentially a return to a strain-hardening mechanism. Vaughan and de Morton suggest that hydrogen forms atmospheres at dislocations more easily than carbon or nitrogen, and that these strain-induced hydrogen atmospheres can maintain contact with moving dislocations, resulting in suppression of yield-point effects.
Recently, French workers\textsuperscript{125} have suggested that the results of Laue back-reflection X-ray measurements on Armco iron before and after hydrogenation show that hydrogen concentrates preferentially around dislocations in the main active (112) slip planes in $\alpha$-iron. The correct interpretation of these results is difficult, and careful experiments by Robertson et al.\textsuperscript{126} have not supported the French work.

A completely different concept of the mechanism of hydrogen embrittlement was proposed by Troiano and his co-workers.\textsuperscript{41} They carried out experiments in which steel specimens of 120 t.s.i. tensile strength were cathodically charged with hydrogen, and then subjected to a short heat-treatment at 150°C to re-distribute the hydrogen. Some of these specimens were then plastically strained to varying degrees at -196°C, following which ductility measurements were made after varying ageing periods at 65°C.

A complex pattern of change in ductility with duration of ageing resulted. With pre-strained material, ductility was initially fairly high and gradually rose to that of unhydrogenated material. A fall in ductility then took place, followed by a final rise. With unstrained material, ductility was low at first, but with increasing time of ageing a slight fall occurred, which was again followed by a final rise. In order to explain these results Troiano and his co-workers postulated that the severity of
of hydrogen embrittlement depends on the combined effect of hydrogen and stress within the metal. They suggested that voids (or lattice imperfections) are able to act as sinks for hydrogen during ageing, especially when their volume is increased by straining, and that hydrogen in the voids is harmless. This accounts for the initial rise in ductility with ageing of pre-strained material. If the voids are conceived as internal notches (on a micro-scale), then when stress is applied, a multi-axial stress system with an associated region of stress triaxiality will be established around each void. Embrittlement is thought to depend on the preferential migration of hydrogen to regions of maximum triaxial stress resulting in a lowering of ductility. The experimentally-observed drop in ductility with further ageing at 65°C can be explained on this basis by assuming that hydrogen diffuses from more distant areas of the specimen to triaxial stress regions. In specimens which were not pre-strained, hydrogen would be expected to concentrate more quickly in the regions of triaxial stress, since the voids would not be enlarged; this accounts for the observed initial fall in ductility on ageing.

There are several unexplained points arising from Troiano's theory. Firstly, it is not postulated whether or not the harmless hydrogen in voids is atomic or molecular. Secondly, there is as yet no explanation for the lowering of the cohesive strength of a perfect lattice by hydrogen. Troiano's voids, however, could
conceivably be equated with the normal imperfections which occur in all metallic lattices, in which case embrittlement would simply be the result of localised super-saturation of the lattice structure with hydrogen. Thirdly, so far as is known, it has not been conclusively shown that hydrogen migrates preferentially to regions of tensile stress.

Recent internal friction work by Hewitt has shown that no internal friction peaks can be obtained from a high-tensile nickel-steel hydrogenated from a hydrogen atmosphere at elevated temperature. It was concluded therefore that the hydrogen was not in interstitial solution in the steel, but was trapped in the neighbourhood of lattice imperfections (e.g. dislocations). The transition temperature above which hydrogen appears to revert to interstitial solution would seem, from diffusion data discussed in Section 2, to be in the region of 130 - 160°C. Hewitt's work thus suggests that hydrogen associated with 'voids' below 130°C is responsible for embrittlement. The main contradictions arising from the theories of Troiano and Hewitt stem from the rather vague definitions of voids and lattice imperfections - if these were more clearly defined it is conceivable that these two theories would appear to be quite similar.
It is now possible to consider the way in which susceptibility to delayed failure is inversely proportional to the rate of hydrogen absorption, as is suggested by the results of the present study. It is possible, of course, that delayed failure of untempered steels might be brought about by a much smaller concentration of hydrogen compared with that required to cause failure of tempered structures; this could be ascribed simply to the higher internal stress present in quenched structures. This does not, however, account for the lower measured hydrogen absorption rate of martensitic REX,539. It should be emphasized here that measurements of hydrogen contents made in the present work are based on the assumption that hydrogen absorbed at room temperature attains a uniform distribution over the entire cross-section of the specimen. The existence of a hydrogen concentration gradient, as postulated by Smialowski\textsuperscript{127}, is far more probable, however, with the bulk of the absorbed hydrogen confined to a thin layer near the surface. A possible interpretation of the present results is that the depth of penetration varies with metallurgical structure. For instance, the relatively short time required for 'saturation' of martensitic REX,539 with hydrogen during cathodic polarization could be accounted for by assuming that martensite is particularly resistant to penetration by hydrogen, due possibly to trapping of hydrogen in lattice defects (voids and dislocations) near the surface. Certainly the concentration of lattice defects is known to increase after quenching.
from high temperature. It could be argued, however, that if lattice defects were the main reason for trapping of hydrogen near the surface, then hydrogen would penetrate further into the steel once the voids and dislocations near the surface became saturated. The resistance to penetration by hydrogen may thus be due simply to the dense, highly distorted nature of the martensite lattice.

Continuing this line of reasoning, increase in hydrogen absorption rate with increase in tempering temperature and the much longer time required for saturation will be associated with the increasing ability for hydrogen to penetrate further into the steel. A possible factor in this connection could well be the breakdown of martensite to Fe$_3$C and ferrite, with the resultant ferrite/Fe$_3$C interfacial area providing relatively easy paths for penetration of hydrogen into the steel interior.

The theory just presented provides a ready explanation for the influence of metallurgical structure on susceptibility to delayed failure. The implication arising from this theory, and from the results on which the theory is based, is that delayed failure is most readily brought about in structures which maintain relatively high concentrations of hydrogen in critical positions (near the surface in martensitic steels, for instance). This hydrogen can then diffuse under the influence of stress to triaxial stress concentrations, and bring about delayed failure in accordance with Troiano's suggested mechanism.
In a recent publication by Berg\textsuperscript{128}, the author suggests that the \( \varepsilon \) -carbide phase which is formed at low tempering temperatures has a strong affinity for hydrogen. This appears to suggest an alternative explanation for the apparently low observed hydrogen absorption rates in lightly tempered structures. Berg has suggested that decomposition of the \( \varepsilon \) -carbide is necessary before occluded hydrogen can be released.

Since decomposition occurs at appreciable rates only at higher tempering temperatures (400°C and above) it was thought that hydrogen occluded by the \( \varepsilon \) -carbide phase in the present experiments might not be evolved by vacuum extraction at 200°C. Several of the cathodically polarized, 200°C-tempered specimens were therefore subjected to a 2-stage extraction procedure; i.e. vacuum extraction at 200°C, followed by extraction at 650°C. No additional hydrogen was detected on increasing the temperature to 650°C, however, and thus retention of hydrogen by \( \varepsilon \) -carbide does not appear to provide an explanation for the present results.

The extremely low hydrogen absorption rate for pure iron measured in the present work is even smaller than that obtained for martensitic REX.\textsuperscript{539}. The implication is that the impurity concentration in the cathode material must be taken into account when considering the hydrogen-absorbing ability of ferrous materials.
This is not surprising in view of the 'poisoning' effect of sulphur, arsenic and other elements on the hydrogen evolution reaction. It is clear from the present work that this poisoning action of arsenic is due to its effect in raising the overvoltage for hydrogen evolution, and that when polarization is carried out potentiostatically with arsenic present in solution, the hydrogen absorption rate does not increase until a 'threshold' overvoltage (about 300 mV) is exceeded. This agrees well with the results of delayed failure tests carried out during cathodic polarization in the presence of arsenic (Section 4.1), when delayed failure did not occur at overvoltages below 300 mV. It is clear, from the $\gamma$/i curves (Fig.22), that the inhibitive action of arsenic on hydrogen absorption is not readily observed during galvanostatic cathodic polarization. (Angestein - Kazlowska$^{129}$ appears to be the only worker who has reported such an effect at low current densities). For a given current density, overvoltage will be raised when arsenic is present (i.e. hydrogen evolution becomes more difficult), and therefore more hydrogen is available for absorption by the steel. This lends further support to the contention, presented earlier, that hydrogen absorption is more dependent on overvoltage than on current density.
SECTION 6. CONCLUSIONS

The experimental work described and discussed in the present work has led to the following conclusions:

1. The vacuum-extraction technique for quantitative determination of very small amounts of hydrogen (≪ 0.1 p.p.m.) absorbed by steel during cathodic polarization in near-neutral solutions is unreliable if the recommended extraction temperature (600°C) is used. Small amounts of atmospheric moisture adsorbed on the metal surface are carried into the heating chamber of the apparatus and can lead to formation of spurious hydrogen, at an extraction temperature of 300°C and above, from a reaction of the type

$$\text{Fe} + \text{H}_2\text{O} \rightleftharpoons \text{FeO} + \text{H}_2$$

which is thermodynamically possible even at low temperatures, or

$$\text{C}_\text{Fe} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}$$

which is only thermodynamically possible above 650 - 700°C.

The extraction of an equal volume of unidentified gas other than hydrogen appears to favour the latter reaction, but the exact mechanism is almost certainly more complex.
A pad soaked in liquid air and situated at the top of the barometric specimen introduction column freezes out most of the moisture and gives some improvement. The technique is quite reliable, however, even without a liquid-air pad, if an extraction temperature of 200°C is employed; complete evolution of hydrogen occluded during cathodic polarization can be achieved in about 45 min., provided that extraction is carried out immediately following polarization.

2. Significant amounts of hydrogen are absorbed by REX.539 steel during cathodic polarization in near-neutral solutions. In the pH range 4 - 6, the quantity of hydrogen absorbed is initially a linear function of duration of polarization; this gradually transforms to 'saturation' conditions, after which time no further hydrogen is absorbed. The initially linear relationship differs from that observed when steel is cathodically polarized in strong acid solutions, when hydrogen absorbed is proportional to $\sqrt{t}$, where $t$ is the time of polarization, in accordance with Fick's diffusion laws. This suggests that the rate of hydrogen absorption from strong acid solutions is diffusion-controlled. On the other hand, the adsorption stage is probably rate-controlling when hydrogen is absorbed during cathodic polarization in near-neutral solutions (pH 4 - 6); a change in the mechanism of hydrogen evolution from electrochemical desorption to slow
discharge as the solution pH is increased would account for this, since slow discharge would give low coverage of the cathode surface with atomic hydrogen. Since the values of the Tafel 'b' for rate-controlling electrochemical desorption and slow discharge hydrogen evolution mechanisms are similar, then observation of the rate of hydrogen absorption by the cathode affords a method of distinguishing between these mechanisms of hydrogen evolution.

3. The amount of hydrogen absorbed during cathodic polarization in de-aerated solutions at pH 4 - 5.5 is directly proportional to overvoltage in the range 50 - 200 mV. This is in accordance with Schuetz and Robertson's observation that

\[
[H]_{\text{ABS.}} = a + b \log i
\]

since

\[
\eta = a + b \log i.
\]

Thus hydrogen absorbed during cathodic polarization is related to the hydrogen evolution reaction. Hydrogen absorbed from solutions of pH greater than 5.5 is no longer proportional to overvoltage; beyond 100 - 150 mV, hydrogen absorption increases only very slowly with increase in over-voltage. This is consistent with hydrogen evolution kinetics, because in near-neutral solutions water molecules provide the
chief source of hydrogen, and direct absorption of protons by the cathode becomes increasingly difficult with rise in pH. The presence of oxygen in solution and inability to control pH leads to non-proportionality between absorbed hydrogen and overvoltage at slightly lower initial pH (i.e. 5.0).

4. The rate of hydrogen absorption by REX.539 is strongly influenced by the presence of impurities, both in the steel and in solution. Potentiostatic studies of REX.539 in solutions containing arsenic showed that hydrogen absorption did not increase until the overvoltage exceeded 300 mV. At lower overvoltages, there is actually a decrease in absorption. This inhibitive region of overvoltage correlates well with the observed disappearance of delayed failure in REX.539 simultaneously stressed in tension and polarized at \( \eta = 100 \) mV. The decrease in hydrogen absorption at low overvoltages is probably due to the inhibiting action of an arsenic-containing species absorbed on the cathode. The increase in hydrogen absorption during galvanostatic polarization in the presence of arsenic is due to an increase in overvoltage for hydrogen evolution, thus favouring the hydrogen entry side-reaction.

The inability of pure iron to absorb significant amounts of hydrogen during cathodic polarization in pure near-neutral solutions emphasizes the role played by impurities in the metal in the process of hydrogen absorption.
5. The rate at which hydrogen is absorbed, and the time taken for 'saturation' with hydrogen to occur, increases with increase in the temperature at which REX.539 is tempered after hardening. This is contradictory to the established behaviour with regard to delayed failure, the propensity to which decreases with increase in tempering temperature. The results can be explained, however, by assuming that hydrogen only penetrates to a limited depth in steel, and that the depth of penetration increases with increase in tempering temperature. Maximum penetration coincides with the appearance in the microstructure of very fine Fe₃C; the large interfacial area between Fe₃C and the ferrite matrix may provide easy paths for penetration of hydrogen into the interior of the metal. The conception of delayed failure must be modified slightly to accommodate the view that the depth of penetration of hydrogen is limited. Since martensite is more susceptible to delayed failure than sorbitic structures, it can be concluded that structures having the most resistance to hydrogen penetration are most easily embrittled, owing to the build-up of large concentrations of hydrogen at dangerous locations. Structures which absorb hydrogen freely will, by the same argument, disperse hydrogen more easily away from possible dangerous locations.
6. The relatively simple sustained tensile-load experiments with notched specimens carried out in the present work show that delayed failure due to absorbed hydrogen is possible in conditions which approximate to those attained in service, when a more anodic metal is in contact with a high-tensile steel. It would be dangerous to place too much importance on the limited number of mechanical tests performed, however, and too many firm conclusions should not be made without a much wider mechanical testing programme.

It is considered that the main contributions made in the present work to the advancement of understanding of the mechanisms of hydrogen absorption and embrittlement of high-strength steels are as follows:

(1) The observation that hydrogen absorbed by REX.539 is linear with duration of polarization in near-neutral solutions, and that hydrogen absorption increases with tempering temperature.

(2) The suggestion that a rate-controlling slow discharge mechanism of hydrogen evolution is operative in near-neutral solutions, as distinct from an electrochemical-desorption-controlled mechanism in strong acid solutions, and the possibility of
distinguishing between these mechanisms by measurement of the Tafel parameter, 'b', in conjunction with determination of the rate of hydrogen absorption.

(3) The conclusion that hydrogen absorption is more strongly dependent on the overvoltage rather than on current density, for hydrogen evolution.

(4) The conclusion that hydrogen only penetrates to a limited depth in hardened and tempered REX.539 during cathodic polarization in near-neutral solutions, and that the depth of penetration increases with increase in tempering temperature.

(5) The proposal, on the basis of the above observations, of a modification to the concept of delayed failure of high-strength steels due to hydrogen.
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FACTORS AFFECTING HYDROGEN ABSORPTION OF HIGH-STRENGTH STEELS DURING CATHODIC POLARIZATION*

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Abstract—A study has been made of hydrogen absorption by high-strength steels during cathodic polarization in intermediate pH solutions using rigidly controlled experimental conditions. Direct hydrogen analysis by the vacuum heating technique has been utilized and it has been established that use of high extraction temperatures (i.e. >400°C) can lead to errors which are probably associated with a reaction between adsorbed water and the steel. Extraction at 200°C has been found to give satisfactory results free from error.

The dependence of hydrogen absorption on the duration of polarization, the potential of the steel and the metallurgical condition of the steel have been studied with a view to establishing whether hydrogen embrittlement may result from the use of coatings of electronegative metals like cadmium and zinc.

INTRODUCTION

It is well known that, under certain conditions, exposure of iron or iron–carbon alloys to a hydrogen containing atmosphere or to an aqueous solution can lead to absorption of hydrogen by the metal. Moreover, it has long been recognized that the presence of hydrogen in these metals can result in loss of ductility of the metal at room temperature.1 This is reflected in reduced values for elongation and reduction in area.

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measured in a normal tensile test. In general, ductility has been shown to be reduced progressively with increasing hydrogen content though a limiting minimum value is reached at a concentration of approximately 4.5 p.p.m. hydrogen above this concentration no further reduction in ductility occurs.

With high strength steels (i.e. having a U.T.S. of approximately 100 ton/in² or more) the presence of hydrogen in the metal can be particularly dangerous because of its ability to cause premature brittle fracture under sustained (static) tensile loads appreciably less than the ultimate tensile strength of the material. This phenomenon is known as "delayed failure" or alternatively "static fatigue".

Hydrogen absorption from electrochemical sources

Many of the chemical and electrochemical treatments used in cleaning and electroplating steels result in reduction of hydrogen ions at the metal/solution interface and consequently may lead to hydrogen absorption by the metal. Thus hydrogen embrittlement has been shown to result from acid pickling or electroplating, particularly during cadmium or chromium plating, of high-strength steels. For this reason, ageing (or baking) treatments at elevated temperature (200°C) to restore ductility to electroplated components are specified.

The possibility that protective coatings such as zinc, cadmium or aluminium may actually result in the introduction of hydrogen into the steel during service cannot be precluded. These metals are electronegative to steel under most service conditions so that at discontinuities in the coating the substrate is cathodically polarized and this may result in entry of hydrogen into the steel.

Reasons for present work

Many investigations have been carried out on absorption of hydrogen from strongly acid and strongly alkaline solutions, mostly with the purpose of developing cleaning and electroplating treatments which give freedom from hydrogen absorption. Some workers have deliberately introduced hydrogen into steel by cathodic charging in strong acid solutions in order to determine the effect of hydrogen on mechanical properties. The importance of factors such as surface finish of the electrode and the presence of impurities in the electrolyte solution on hydrogen absorption has sometimes been overlooked in such studies with the result that reproducibility has suffered. In addition, embrittlement has often been evaluated solely by mechanical tests and little attention has been given to the accurate quantitative determination of amounts of hydrogen absorbed.

In contrast to numerous studies carried out in acid solutions, very little information on hydrogen absorption from solutions of intermediate pH (i.e. pH 4–9) appears to be available. It was felt, therefore, that a study of factors influencing hydrogen absorption (measured by direct analysis) of high-strength steels during cathodic polarization in solutions of intermediate pH would be of interest. In addition, cathodic polarization at near-neutral pH values would tend to simulate conditions which could arise in service when steel is coated with a galvanically less noble metal. The present investigation describes the effect of the following factors on hydrogen absorption of cathodically polarized high strength steel:

1. Electrode potential of the steel.
(2) Duration of polarization.
(3) Metallurgical condition of the steel.

EXPERIMENTAL TECHNIQUES

(a) Materials
REX.539 high-tensile steel rod $\frac{3}{8}$ in. diameter (supplied by Firth Brown) was used for most experiments. A typical analysis is as follows: 0.38 C, 1.5 Si, 1.5 Mn, <0.020 S, <0.020 P, 1.75 Ni, 0.4 Mo, 0.2 V.

A limited number of experiments were also performed with spectrographically standardized iron rod (impurities <0.001 per cent) in the fully annealed condition.

(b) Specimen preparation
Austenitizing in an argon atmosphere at 865°C and oil quenching followed by tempering in vacuum was used to give tensile strengths in the range 80–130 ton/in².

All specimens were machined to a diameter of 0.200 in. and a length of 1.2 in.; in the case of high-tensile steel specimens grinding to final dimensions was carried out after heat treatment. The surface was then abraded with successively finer silicon carbide papers and polished with Hyprez diamond compound, finishing with 1 $\mu$ particle-size diamond. Specimens were finally stress-relieved at 200°C in vacuum.

Treatment in aqueous solutions was avoided owing to the possibility of introducing hydrogen, and after degreasing in acetone and drying in hot air the specimens were used directly for cathodic polarization studies.

(c) Cell
An all-glass cell (Fig. 1) was used for polarization studies and to avoid possible contamination by rubber the cylindrical steel specimen (cathode) was supported in the glass syringe by a p.t.f.e. sleeve. The cell was enclosed in an air thermostat enabling a constant temperature of 25 ± 0.5°C to be maintained. A platinum anode was used and provision was made for passing a rapid stream of de-oxygenated argon through the electrolyte in both anode and cathode compartments in order to ensure that oxygen liberated at the anode did not diffuse to the cathode and cause depolarization of hydrogen discharge. Argon was first passed through a modified "Nilox" scrubber (Fig. 2), containing chromous sulphate solution and zinc amalgam, to remove trace amounts of oxygen from the gas.

In order to prevent oxygen evolution some experiments were carried out using a large hydrogen electrode as the anode and it was demonstrated that the results obtained for hydrogen uptake at the cathode were the same as when a platinum anode was used. This showed that the procedure for removing oxygen from the anode by means of argon was effective.

(d) Solutions
AnalaR chemicals and doubly distilled water were used for all experiments. The solution was first de-oxygenated in a scrubber in series with the gas-purifying scrubber, and then pumped over into the main cell under a pressure of purified argon.

Preliminary experiments were performed with an 0.5 M solution of sodium
sulphate. Chloride solutions were not used because hypochlorite formed at the anode would act as electron acceptors at the cathode. Later it was realized that pH control was important and for this reason subsequent polarization experiments were carried out using a sodium acetate-acetic acid buffer. Experiments were confined mainly to pH 4.0 and the effect of the other variables were investigated at this pH.

(e) Electrochemical measurements

Both potentiostatic and galvanostatic techniques were employed in polarization experiments. Potentiostatic studies were carried out with a sensitive potentiostat (Witton Electronic Ltd, made to specification) which controlled the potential to ± 2 mV during short-term experiments and ± 5 mV during more prolonged experiments (24 hr). Galvanostatic experiments were performed with an electronic constant current device.

Potentials were determined with a mercury/mercurous sulphate reference electrode ($E^{\circ}_{25^\circ C} = 0.615$ V) and Luggin capillary which was placed 1 mm away from the
f) Hydrogen estimation

The method used for estimating the hydrogen absorbed was similar to that described by Sloman. The steel was heated in vacuum and the hydrogen evolved was determined volumetrically. Direct introduction of the specimen into the previously evacuated apparatus was effected by means of a mercury air-lock using a magnet to manipulate the specimen into the furnace tube. Hydrogen diffused out of the specimen rapidly at the elevated temperatures used and was collected and measured and then removed by diffusion through an external palladium thimble heated at 500°C. A sensitivity of 0.01 p.p.m. by weight hydrogen was achieved with this method.
Since the investigation was concerned with the effect of certain factors on hydrogen absorption (as outlined earlier) it was necessary to select an arbitrary "standard" set of conditions for all polarization experiments. The "standard" conditions chosen were as follows:

1. REX.539 steel oil-quenched and tempered at 600°C (1 hr); standard surface preparation (see b).
2. Acetate/acetic acid buffer (pH 4.0).
3. Overpotential of cathode 100 mV (for potentiostatic experiments).
4. Duration of polarization 3 hr.

Each of the above conditions was varied independently so that the effect of each factor on the absorption of hydrogen could be determined. In all polarization experiments the open-circuit potential of the steel was measured prior to polarization. This potential, which was pH dependent ($E = -0.330$ V at pH 4 and $-0.395$ V at pH 5), was found to attain a steady value after 3 min and the reproducibility of the potential at the steady state was $\pm 5$ mV.

RESULTS

Influence of extraction temperature on hydrogen estimation

Before studying the effect of the different variables on hydrogen absorption it was necessary to ascertain the most suitable temperature for hydrogen extraction. Gas evolution experiments were performed at various temperatures from 200-700°C using REX.539 steel both in the "as received" condition (Fig. 3) and after cathodic polarization in 0.5 M sulphuric acid (Fig. 5).

Figure 3 shows that the hydrogen evolved increases with temperature and with time although at 200°C the effect of time of extraction is negligible. This result was unexpected as results of previous work indicated that in view of the small specimen size (0.2 in. dia.), complete extraction should be achieved in 20–30 min. With "as received" specimens very little hydrogen could be detected if extraction was performed below 400°C. Since the "blank" rate of the apparatus was negligible these results appear to confirm the results of Brittain who has shown that adsorbed moisture on the specimen can react with steel (or carbon in steel) giving hydrogen. Results obtained at successively higher temperatures on specimens which had been previously heated in vacuum for 5 hr at 700°C and then exposed to the atmosphere before hydrogen estimation (Fig. 4) appear to confirm this view. Whether the effects observed at elevated temperatures are due to this reaction, or to the escape of molecular hydrogen, or to slow evolution of atomic hydrogen in a relatively immobile form is still, however, controversial.

It is apparent from these results (Figs. 3 and 4) that hydrogen contents measured by vacuum extraction at and above 600°C should be viewed with caution, especially where the expected hydrogen content is below 0.25 p.p.m.

Results obtained on REX.539 specimens cathodically polarized in 0.5 M sulphuric acid at 0.2 mA/cm² for 1 hr followed by hydrogen determination at different temperatures are shown in Fig. 5. These indicate that all of the hydrogen absorbed by steel during polarization is evolved in about 45 min during vacuum extraction at 200°C. At higher temperatures the hydrogen evolved increases with time. Since it is the more
Factors affecting hydrogen absorption of high-strength steels during cathodic polarization

Fig. 3. Hydrogen evolved from "as received" REX.539 steel at different extraction temperatures.

- 700°C; ● 600°C; □ 500°C; ■ 400°C; Δ 200°C.

Fig. 4. Hydrogen evolved from vacuum annealed (5hr at 700°C in vacuum followed by exposure to the atmosphere) "as received" REX.539 steel at different extraction temperatures.

- 700°C; ● 600°C; □ 500°C; ■ 400°C; ▼ 300°C; Δ 200°C.
mobile type of hydrogen (extractable at 200°C) which is now thought to be responsible for embrittlement this result is of practical importance as it means that high-temperature extraction is neither desirable nor necessary, and results obtained by vacuum extraction at 200°C appear to be more significant than those obtained by extraction at high temperatures. Consequently low-temperature extraction has been adopted throughout the present work.

**Dependence of hydrogen absorption on polarization time (duration)**

Potentiostatic experiments were performed on REX.539 for times up to 20 hr using the “standard” conditions of potential and pH. Typical results for three tempering temperatures are shown in Fig. 6.

In general, these curves show an initial linear increase with time but ultimately become approximately horizontal. The time beyond which the curves deviate from linearity varies with tempering temperature, being longer for high tempering temperatures (e.g. 10 hr at 600°C) and shorter at low tempering temperatures (e.g. 3½–4 hr at 200°C). The horizontal portion on each curve probably represents the saturation concentration of hydrogen in steel for the given experimental conditions.

**Dependence of hydrogen absorption on potential or charge**

Potentiostatic and galvanostatic techniques were used to determine the dependence of hydrogen absorption (REX.539 and acetate buffer, pH 4.0) on cathode overvoltage (\(\eta\)) and current density. It is evident from the results (Figs. 7 and 8) that the quantity of hydrogen absorbed increases linearly with \(\eta\) for overvoltages between 50 and 200 mV, and with \(\log i\) for current densities between 0.1 and 2.5 mA/cm². It
Factors affecting hydrogen absorption of high-strength steels during cathodic polarization

Fig. 6. Effect of time of cathodic polarization on hydrogen content of hardened REX.539 steel tempered at different temperatures (acetate buffer pH 4-0; overvoltage 100 mV).
- tempered at 600°C;
- tempered at 400°C;
- tempered at 200°C.

Fig. 7. Effect of overvoltage and tempering temperature of hydrogen content (hardened REX.539, tempered at different temperatures, time of cathodic polarization 16 hr).
- pH 4: ○ tempered at 600°C; ● tempered at 400°C; □ tempered at 200°C.
- pH 6: ■ tempered at 600°C.
Fig. 8. Relationship between hydrogen absorbed and log $i$ (hardened REX 539, acetate buffer pH 4.0, polarized 3 hr).
- ○ tempered at 600°C; ● tempered at 400°C; □ tempered at 200°C

Fig. 9. Effect of tempering temperature on absorption of hydrogen (hardened REX 539, acetate buffer pH 4.0, overvoltage 100 mV, polarization time 16 hr).
Factors affecting hydrogen absorption of high-strength steels during cathodic polarization

Fig. 10. Overvoltage-time curves at constant current (hardened REX 539, acetate buffer pH 4.0, c.d. 0.20 mA/cm²).

- untempered; ○ tempered at 600°C; ● tempered at 400°C;
■ tempered at 200°C. For comparison ▼ shows annealed pure iron.

should be observed that no absorbed hydrogen could be detected in unpolarized specimens which had been immersed for 24 hr in the buffer solution at pH 4.

Results of potentiostatic experiments carried out at pH 6.0 are also shown in Fig. 7, curve 4. This result differed from that obtained at pH 4.0 as increasing the overvoltage above 125 mV did not result in a further increase in absorbed hydrogen.

Dependence of hydrogen absorption on metallurgical structure

The amount of hydrogen absorbed during cathodic polarization of REX.539 steel (“standard” conditions) tempered at temperatures from 100–600°C has been measured, and the results are summarized in Fig. 9. These results confirm those given in Figs. 6–8 and show that the rate of hydrogen absorption is markedly increased with increase in tempering temperature.

It should be observed that studies of pure iron showed that very little hydrogen was absorbed when the iron was cathodically polarized under the “standard” conditions which produced rapid absorption of hydrogen by the high-tensile steel.

Galvanostatic experiments, in which the variation of overvoltage with time was observed (Fig. 10), showed a steady rise in overvoltage to an apparent maximum for REX.539 tempered at 600°C, but a pronounced drop in overvoltage for tempering temperatures of 400°C and below. Pure iron also exhibited a drop in overvoltage. This change of overvoltage with time seems to depend markedly on the ability of the material to absorb hydrogen.
DISCUSSION OF RESULTS

The present work represents a preliminary study of some of the factors which affect the rate of hydrogen absorption during cathodic polarization of a typical high-tensile steel in an aqueous solution. The experimental conditions chosen have been based to some extent on the conditions which could prevail at a steel surface which is partly coated with a more electro-negative metal and, for example, it has been established that coupling REX.539 with cadmium in neutral 3 per cent NaCl results in a depression of the steady-state potential of the steel by ~ 50 mV. Although near-neutral solutions, which are more significant for service conditions than the strongly acid solutions used for deliberate charging of steel with hydrogen, have been used they have the disadvantage that pH changes occur at the cathode during evolution of hydrogen; for this reason acetate/acetic acid buffers rather than neutral chloride solutions have been selected for these studies.

In the present study potentiostatic conditions have been preferred in the majority of experiments to galvanostatic conditions as it is considered that they represent a more fundamental approach to the problem and have greater practical significance. The true current density requires a knowledge of the true surface area which in turn depends upon surface preparation and it is far simpler in practice to measure a potential than a galvanic corrosion current. From a fundamental viewpoint an increase of the cathodic overvoltage should result in an increase in the hydrogen atom concentration.

The experimental conditions of charging have been rigidly controlled and attention has been paid to solution purity with particular reference to the exclusion of oxygen. Under the conditions described it has been shown that the introduction of hydrogen into a high-tensile steel during cathodic polarization is highly reproducible, and that hydrogen introduced electrochemically can be removed from the steel at temperatures as low as 200°C. High temperatures have been shown to be undesirable owing to possible errors which may arise owing to reaction of absorbed water vapour with the steel—a possibility which cannot be discounted under most experimental conditions of hydrogen estimation.

Parallel studies on the effect of hydrogen on mechanical properties have not been made so that the hydrogen absorption rates reported are not necessarily indicative of delayed failure.

It is well known that the hydrogen evolution reaction occurs by a series of steps and that, depending on the particular system, any one (or more) of these steps may be rate-determining. The Tafel equation is applicable when the rate of the reverse reaction (ionization of hydrogen gas) can be neglected, i.e. when the overvoltage is > 50 mV and, under these conditions, \( \eta = a + b \log i \) where \( a \) and \( b \), the Tafel parameters, may be diagnostic of the rate determining step. A review of Tafel parameters in relation to the mechanism of the hydrogen evolution has been given by Barton.

These steps can be summarized as follows:

\[
\begin{align*}
\text{diffusion} & \quad \text{discharge} & \quad \text{combination} \\
\text{migration} & \quad \text{dehydration} & \quad \text{(c)} \\
\text{convection} & \quad \text{(a)} & \quad \text{(b)} & \quad \text{(d)} \\
(H_3O)^+_{\text{sol.}} & \rightarrow (H_3O)^+_{\text{elect.}} & \rightarrow M - H & \rightarrow M - H + (H_3O)^+ + e \rightarrow H_2 \\
& & \text{or electrochemical} & \\
& & \text{(c)} & \\
& & \text{(d)} & 
\end{align*}
\]
It is evident that any discussion of the entry of hydrogen into metals must involve a consideration of the mechanism of the hydrogen evolution reaction of the particular system under consideration. However, it is necessary to point out that studies have, in general, been confined to strongly acid or strongly alkaline solutions. The reason for this is not surprising as, in the neutral region, pH changes at the metal/solution interface with the consequent possibility of alternative reactions may complicate the interpretation of results. Thus Bockris has shown that the reduction of the hydronium ion and water become energetically equal at pH 8 so that reduction of both species to hydrogen occurs simultaneously.

Further, it is necessary to observe that the nature of the surface of the cathode is of the greatest significance in the mechanism of the hydrogen reaction and the Tafel parameters available for pure iron cannot be applied to the martensitic and sorbitic structures of the high-tensile steel used in the present work. Thus, under the conditions used in the present study, little hydrogen enters pure iron during cathodic polarization whereas appreciable quantities are absorbed by the high-tensile steel when in the fully tempered condition.

In considering the various rate-determining steps it is possible, in view of the low currents and conditions of turbulence used in the present study, to disregard diffusion of hydronium ions to the cathode surface as a possible rate-determining step. In addition, the concentration of hydrogen molecules adsorbed on the surface of a cathode is considered to be negligible for all mechanisms except hydrogen discharge on highly activated platinum. Once hydrogen gas is evolved $p_{H_2} = 1$ atm and although an increase of overvoltage will increase the rate of evolution of hydrogen gas it will not alter the hydrogen potential. The fact that hydrogen does not enter as molecules is confirmed by the observation that an increase of overvoltage increases the rate of absorption of hydrogen (Fig. 7). This is supported by the fact that gas phase studies have indicated that the species present in the metal are monatomic.

Whether the hydrogen is introduced into the steel as protons or atoms is still not clear. It is evident, however, that the species which enters will be adsorbed on the metal surface and is likely to be present there in reasonably high concentrations. The rate-determining step of the over-all hydrogen reaction will determine the surface coverage of adsorbed atoms and consequent introduction of the hydrogen species into the metal. Thus, if atomic combination is rate-determining (step c) hydrogen atoms will remain adsorbed on the metal and surface coverage will be complete. If the discharge reaction (step b) is rate-determining, the coverage will be low. The rate-determining step may have a bearing, therefore, on the nature of the species which enters the steel.

For the present purposes it will be assumed that the species which enters the metal is the hydrogen atom, and the entry of this species into the metal can be regarded as a side-reaction which accompanies a step in the over-all process in which surface coverage of the cathode by this species is relatively high. No postulates can be made as to the mechanism of the hydrogen reaction on the high-tensile steel studied, but it is evident that the rate-determining step must be different from that on pure iron. It is also evident that the mechanism will differ according to the pH prevailing at the cathode surface and that any impurity which affects the rate of a step in the over-all process will also affect the absorption rate.
Hydrogen entry into metal

It has been suggested that the rate of absorption of the adsorbed protons or hydrogen atoms by the electrode will depend on the rate of diffusion of hydrogen (irrespective of form) into the electrode material. Darken and Gurry have shown that if the rate of hydrogen absorption is diffusion-controlled and conforms to Fick's Laws then the concentration of hydrogen in steel, for periods of time shorter than that required for saturation (Fig. 6), should be proportional to the square root of the exposure time. Thus Schuetz and Robertson have established a linear relationship between absorbed hydrogen and \( t^{1/2} \) for steel cathodically charged in sulphuric acid or in an aqueous solution of hydrogen sulphide. It should be mentioned, however, that their results show considerable scatter. The linear dependence of hydrogen absorption on \( t \) which has been observed in the present study over a limited range of \( t \) during cathodic polarization in buffer solutions of intermediate pH does not support arguments based on Fick's Law. Diffusion of hydrogen into steel at room temperature does not necessarily conform with Fick's Law and several workers have put forward evidence which shows deviations. Thus Hobson during measurements of the rate of hydrogen evolution from steel in the temperature range 78 to 200°C observed much lower values for the diffusion coefficient than those extrapolated from results of high temperature measurements.

Although at high pressures of hydrogen the assumption that hydrogen completely covers the surface is valid, this is not necessarily the case at low pressures, or during entry of hydrogen from aqueous solution. In the case of the latter the coverage of the surface by the species which enters the metal is not necessarily complete and can vary with time during polarization. Under these circumstances, the rate of adsorption on the metal surface rather than diffusion into the metal, may be rate determining.

The observation that the saturation concentration appears to differ markedly for different specimens of the same material under the same experimental conditions is consistent with previous work. This is shown by the scatter of values obtained after 15 hr at 600°C (Fig. 6). Schuetz and Robertson also refer to the phenomenon of “apparent supersaturation” in which the linear absorption rate with respect to \( t^{1/2} \) extends significantly beyond the ultimate saturation limit. This has also been observed in the present work and it can be seen (Fig. 6, 600°C) that one of the results shows a hydrogen content which is well in excess of the apparent saturation limit.

Dependence of hydrogen absorption on overvoltage and current

Figure 11 shows that the high tensile steel used in the present study under standard conditions (pH 4) gives a Tafel relationship with \( b = 0.17 \). In addition, it can be seen that hydrogen absorption varies linearly with overvoltage (\( \eta \)) or with log \( i \) and this suggests a relationship between the mechanism of the hydrogen evolution reaction and rate of absorption. A similar conclusion was reached by Schuetz and Robertson for absorption from strongly acid solutions. At high pH values (pH 6–7) a linear relationship between rate of hydrogen absorption and overvoltage is not obtained (Fig. 7). This is probably due to a change in the mechanism of the hydrogen evolution reaction in this range where the pH at the cathode may be sufficiently high for water as well as the hydronium ion to be reduced to hydrogen. Barton suggests that the tendency for some metals to change to a slow discharge mechanism in alkaline
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![Graph showing overvoltage-log i curve](image)

**Fig. 11.** Overvoltage-log $i$ curve (hardened REX 539 steel, tempered 600°C, acetate buffer pH 4–0).

solutions with a resultant low coverage of the surface may also explain the lower permeation rate of hydrogen at elevated pH values.

From a practical viewpoint this is of interest as it shows that alkali formed at the cathode may be a significant factor in preventing entry of hydrogen and consequent delayed failure. This was confirmed by cathodically polarizing REX.539 in a boric acid/sodium hydroxide buffer solution of pH 8–10, when very low hydrogen absorption rates were found.

It should be observed that no hydrogen could be detected in a REX.539 specimen after 10 hr immersion in a buffer at pH 4 without polarization, whereas Darken\(^2\) found that appreciable amounts of hydrogen were absorbed by a plain carbon steel exposed to similar conditions.

**Dependence of hydrogen absorption on metallurgical structure.**

From Figs. 6 and 9 it would appear that metallurgical structures having a finely dispersed Fe$_3$C precipitate in a ferrite matrix (i.e., resulting from tempering at 600°C) absorb hydrogen at a greater rate than structures consisting of partially tempered martensite produced by low tempering temperatures. At first sight this seems surprising since structures which contain martensite show a much greater susceptibility to hydrogen embrittlement than sorbitic structures. The added complexity of internal stress should be taken into account, however, when considering the effect of hydrogen on a given metallurgical structure. It may be possible that a much smaller concentration of hydrogen is needed to cause delayed failure of untempered steels compared to that required for a fully tempered structure.

With reference to the inability of fully annealed pure iron to absorb electrochemical hydrogen in significant amounts, it seems probable that hydrogen absorption is governed essentially by factors such as impurities, internal stress (giving a high disloca-
tion density) or a two-phase metallurgical structure. In connection with the latter factor, it is possible that the ferrite/Fe₃C interfacial area may have some influence on hydrogen absorption.

In a recent publication by Berg, the author suggests that the ε-Fe₃C phase, which is formed at low tempering temperatures, has a strong affinity for hydrogen. This appears to suggest another possible explanation for the results of Figs. 6 and 9. Berg has suggested that decomposition of the ε-carbide is necessary before occluded hydrogen can be released. Since decomposition occurs at a rapid rate only at higher tempering temperatures (i.e. 400°C and above) it was thought that hydrogen occluded by the ε-Fe₃C phase in the present experiments might not be evolved by vacuum extraction at 200°C. Several of the 200°C tempered specimens were therefore subjected to a two-stage extraction procedure, i.e. vacuum extraction at 200°C followed by extraction at 650°C. No additional hydrogen was detected on increasing the temperature to 650°C, however, and the retention of hydrogen by ε-Fe₃C does not provide an explanation of the present results.

It would appear from Fig. 10 that it is kinetically easier to discharge hydrogen on steel tempered at low temperatures and it follows, therefore, that the side-reaction on these steels (i.e. entry of hydrogen) will be less significant. This is in agreement with the results of galvanostatic experiments in Fig. 8.

CONCLUSIONS

The following conclusions can be drawn on the absorption of hydrogen by REX.539.

1. Hydrogen analysis by vacuum extraction at 600°C and above may be liable to error due to reaction between moisture and the specimen especially where the hydrogen content is < 0.25 p.p.m. and where the steel specimen is introduced into the apparatus through a mercury column. Extraction at 200°C immediately after cathodic polarization gives complete evolution of all hydrogen absorbed during polarization.

2. Hydrogen absorption of REX.539 from buffered acetate solutions of pH 4 is approximately linear with time. Linearity persists up to 4 hr for specimens tempered at 200°C, and up to 10 hr for a tempering temperature of 600°C. With greater times the absorption/time curves change gradually from a linear slope to the horizontal portion which corresponds with saturation.

3. The relationships between hydrogen absorption and η and likewise hydrogen absorption and log i are linear, at least for values of η between 50 and 200 mV, and for i values between 0.1 and 2.0 mA/cm².

4. The higher the tempering temperature the greater is the rate of absorption of hydrogen (i.e. martensitic-type structures have a lower absorption rate than tempered structures). In addition, the course of η/t curves obtained at constant current depends markedly on the ability of the electrode material to absorb hydrogen.

Without adequate mechanical tests, it is extremely difficult to say whether the amounts of hydrogen absorbed by REX.539 during cathodic polarization in intermediate pH solutions will be sufficient to cause embrittlement. Certainly the amounts appear small, but it should be remembered that these amounts represent average concentrations extracted from a relatively large volume of steel. It is possible that much higher local concentrations of hydrogen may be present (particularly at the surface)
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which may well be sufficient to cause embrittlement. Unfortunately the techniques used in the present study are incapable of providing information about the possibility of local high concentrations, which are most likely the determining factor in embrittlement rather than the overall average concentration.

There is considerable scope for further work in connection with this problem and at the present time work is being continued on the effect of metallurgical condition of the steel. Studies of the Tafel relationships on heat treated steels of practical importance may lead to a correlation between the mechanism of the hydrogen evolution reaction and absorption of hydrogen by the steel.

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REFERENCES