Hydrogen Embrittlement of Steel
Review of the Literature
Heat Treatment and Properties of Iron and Steel

This publication presents basic theoretical and practical principles involved in the heat treatment of ferrous metals.

The effects of various treatments on the structural and mechanical properties of iron and steel are thoroughly discussed, although many theoretical aspects and technical details have been omitted for the sake of simplicity. Subjects presented include properties of iron, alloys of iron and carbon, decomposition of austenite, heat treatment of steels, hardenability, heat treatment of cast iron, nomenclature of steels, recommended heat treatments, and properties and uses of steels. A list of selected references is also given, and a large number of graphs, tables, and photographs illustrate the text.


Nickel and Its Alloys

This publication is a systematic and readily accessible summary of information about nickel. Information obtained by the Bureau in its own investigations is combined with that available in published records of work done elsewhere.

Information includes sources of nickel; extraction, recovery, and refining processes; metallography; chemical properties; physical properties; mechanical properties at different temperatures; and casting, fabrication, and miscellaneous processes. Many ferrous and nonferrous alloys are listed, and their properties, such as density, thermal conductivity, tensile strength, magnetic properties, and corrosion resistance are discussed.

Hydrogen Embrittlement of Steel

Review of the Literature

R. W. Buzzard and H. E. Cleaves

National Bureau of Standards Circular 511

Issued September 24, 1951
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Chemistry of the hydrogen-iron system</td>
<td>2</td>
</tr>
<tr>
<td>2.1. Absorption</td>
<td>2</td>
</tr>
<tr>
<td>2.2. Diffusion</td>
<td>3</td>
</tr>
<tr>
<td>2.3. Solubility</td>
<td>3</td>
</tr>
<tr>
<td>2.4. Evolution and removal of hydrogen</td>
<td>3</td>
</tr>
<tr>
<td>3. Effect of hydrogen on the properties of iron</td>
<td>4</td>
</tr>
<tr>
<td>3.1. Structure, physical, and mechanical properties</td>
<td>4</td>
</tr>
<tr>
<td>3.2. Chemical properties</td>
<td>4</td>
</tr>
<tr>
<td>4. Embrittlement caused by hydrogen from different sources</td>
<td>5</td>
</tr>
<tr>
<td>4.1. Hydrogen absorbed by molten metal</td>
<td>5</td>
</tr>
<tr>
<td>4.2. Hydrogen absorbed or retained by solid steel</td>
<td>7</td>
</tr>
<tr>
<td>4.3. Hydrogen absorbed in chemical reaction</td>
<td>11</td>
</tr>
<tr>
<td>5. Summary</td>
<td>13</td>
</tr>
<tr>
<td>6. Selected bibliography</td>
<td>14</td>
</tr>
</tbody>
</table>
Hydrogen Embrittlement of Steel

Review of the Literature

R. W. Buzzard and H. E. Cleaves

A review of the literature establishes the fact that steel absorbs hydrogen on exposure to the gas at an elevated temperature or in the environment of a chemical reaction. Initial concern of hydrogen so absorbed centered in the tendency to cause porosity and blowholes in the cast metal. Subsequently the list of defects attributed to hydrogen was greatly enlarged to include flaking, pickling embrittlement, shatter cracks, hairline cracks, weldment failures, and numerous other service failures. The data presented in the literature fail to establish quantitative proof that hydrogen is the sole cause of these defects, but it is well established that when procedures for maintaining the hydrogen content at a minimum are utilized, certain defects generally ascribed to hydrogen can be eliminated.

1. Introduction

Gases have long been held responsible for many of the service failures of ferrous materials. Formerly, failures attributed to gas were largely ascribed to oxygen, but with the gradual accumulation of evidence that oxygen is not a major factor in producing most of these defects, the blame has been shifted to hydrogen. General opinion now is that hydrogen embrittles steel.

In general, the hydrogen embrittlement of steel develops a condition of low ductility after exposure to a hydrogen environment, that is, one containing hydrogen gas or chemically combined hydrogen. Because all steels are exposed at one time or another to an environment containing hydrogen, arguments have been advanced blaming all brittle fractures on hydrogen. The probability of hydrogen being the cause of embbrittlement of steel is argued by others to be very exceptional. However, laboratory experiments have shown that hydrogen can cause brittleness, and improvements in methods of analysis have made it possible to show an apparent relationship between brittleness and hydrogen content.

The low ductility of steel attributed to hydrogen may be manifested by either macroscopic cracks, which have been termed “flaking,” “hairline cracks,” “shatter cracks,” etc. or by other manifestations as encountered in “pickling-embrittlement” and “hydrogen embrittlement.” Attempts to classify hydrogen embrittlement defects on the basis of their physical appearance have led to confusion and disagreement between investigators. The nomenclature thus developed may represent not different types but different aspects of the same type failure, produced by the identical hydrogen reaction. A classification based on visual inspection of the defect tends to develop a terminology reflecting the individuality of the investigator. In making the present review it was found that results of many investigators could be organized better by
classifying the defects according to the probable source of the hydrogen in the metal rather than the more generally used descriptive terms based on visual examination.

Hydrogen found in solid steel may be (a) that portion of the hydrogen dissolved in molten steel that is retained after solidification, (b) hydrogen introduced by exposure of the solid steel to a hydrogen environment at elevated temperatures, or (c) hydrogen introduced during chemical or electrochemical treatments. In this paper (a) will be identified as “hydrogen of fusion,” (b) as “thermal hydrogen,” and (c) as “nascent hydrogen.” A classification such as this emphasizes the source of the retained hydrogen rather than the appearance of the resulting defect. Defects generally associated with “flaking” are usually induced by “thermal hydrogen” and “hydrogen of fusion,” whereas “pickling embrittlement” is associated with “nascent hydrogen.”

It should not be inferred that there are three distinct types of hydrogen nor that the defects, regardless of source, may differ other than in degree. The miscellaneous phenomena known as flakes, shatter cracks, pickling embrittlement, etc., will be considered specific degrees of hydrogen embrittlement. Probably the chemical reactions involved are characteristic of the source of the hydrogen and influence the resultant defect. For this reason the review of the embrittlement of steel by hydrogen will be preceded by a brief review of available information on the chemistry of the hydrogen-iron system and the effect of hydrogen on the structure and properties of iron.

2. Chemistry of the Hydrogen-Iron System

2.1. Absorption

The absorption of hydrogen by iron is a complicated process of adsorption of hydrogen at the surface of the iron, diffusion of adsorbed hydrogen into the iron, mechanical retention of hydrogen in discontinuities, and solution of hydrogen in the iron. Differences in the effect of variables on each of these phenomena and their influence under different conditions further complicate the process of hydrogen absorption.

Hydrogen in solid iron forms an interstitial type solid solution, that is, the hydrogen atoms are distributed uniformly throughout the crystal lattice of the iron. Its characteristics in iron are, in general, not analogous to those elements whose diffusion characteristics are easily observed. Unlike carbon, nitrogen and oxygen, hydrogen does not form iron compounds: hence its penetration is not readily studied.

The relation of purity of the iron to absorption of hydrogen is controversial. Some investigators have reported that high purity iron did not absorb hydrogen and that the presence of substantial amounts of impurities in the iron is necessary to cause absorption of hydrogen (527, 542, 1076), whereas other investigators report that iron of equally high purity did absorb hydrogen (947, 1115). The purity of the iron cannot be held to be the sole factor controlling absorption; other variables such as the purity of the chemicals used in making pickling solutions or the surface condition of the iron may be equally important.

Small differences in procedure by which hydrogen is introduced into iron may influence absorption phenomena (173, 368, 758, 947). The absorption of hydrogen gas by iron begins in the vicinity of 400°C (75, 138, 139, 363, 390, 453, 463A, 481, 482, 513, 574, 577, 624, 625, 647, 682, 778, 790, 795, 807, 850). The amount of hydrogen inherited from the melt (hydrogen of fusion) may be affected by variations in the melting operation such as mechanical stirring or mixing of the melt and by impurities. Nascent hydrogen, for example, from pickling and electrolysis, exhibits many effects not observed with either hydrogen of fusion or thermal hydrogen.

Adsorption, the first phase of hydrogen absorption, may be classified as physical or activated (chemi-adsorption) (523). The class encountered is determined by the temperature of the system (363, 514, 520, 522, 523, 546, 548, 669, 677, 791), and physical adsorption of hydrogen by iron normally occurs only at relatively low temperatures.

Adsorption data have been obtained largely on fine aggregates of questionable purity (363, 522, 523, 840). Chemisorbed hydrogen undergoes dissociation on heating and may exhibit fairly well defined decomposition temperatures. The process leads to formation of surface compounds which may be superficial or intercrystalline. The chemisorbed layers have lateral movement and permit adsorption of super-imposed layers (633A). Fresh metal surfaces are relatively high in adsorption power but all areas of a surface are not equally active in adsorbing gas. There

---

1 Figures in parentheses refer to the literature references in the bibliography at the end of this Circular.
is some evidence that the active points correspond to the edges of crystals at grain boundaries or faults (195, 683).

2.2. Diffusion

Diffusion, the movement of hydrogen within the metal, is the second step included in the general term “absorption.” Adsorbed hydrogen diffuses into the metal interstitially, according to Seitz (1024). Diffusion of hydrogen through iron conforms to the general equation derived from the kinetic theory, based on the assumption that the phenomenon is chemical in nature (778). The rate of diffusion of hydrogen varies as the square root of the pressure (5, 8, 15, 21, 49, 89, 91, 110, 195, 260, 303, 311, 363, 390, 482, 513, 522, 542, 574, 606, 694, 711, 712, 748, 773, 790, 795, 807, 859, 877, 896, 939, 981, 1005, 1024, 1036). Absorption at 100°C has been ascribed to diffusion along both grain boundaries and planes of weakness (514, 520) others assume movement is only along planes of weakness (788, 1150). The rate of diffusion differs for the different allotropic forms of iron (576, 639, 661, 711, 712, 778, 792, 824, 882, 998, 1064) but grain size apparently exerts little effect (303, 304, 390, 563, 576, 616, 684, 697, 758, 795, 824, 939). There is evidence of a tendency toward anisotropy, especially in cold-worked structures (463A, 928). It has been suggested that diffusion of hydrogen in a metal occurs in two distinct ways: (1) preferentially, along the slip planes and intercrystalline spaces, and (2) general, through the lattice (633A). Investigators concur in the opinion that hydrogen concentrates on the cleavage planes (367, 788, 1150).

The term “permeability” is often used as though synonymous with diffusion but more generally includes the combined stages of absorption, diffusion and evolution. Most hydrogen diffusion data are derived from permeability data, as the rate of diffusion in the metal is too rapid for measurement. The variables affecting permeability, however, are not necessarily applicable to diffusion.

The permeability and diffusion of hydrogen through metals both rise with rising temperature (50, 110, 173, 241, 378, 576, 661, 683, 684, 711, 712, 778, 792, 824, 882, 998, 1064). Nascent hydrogen released at the liquid-metal interface, as in an electrolytic cell, may introduce large volumes of hydrogen into the metal, and development of a high hydrogen pressure at the interface has been offered as an explanation of the high permeability rates observed on electrolysis. Some data on the effect of applied pressure on the permeability by thermal hydrogen or hydrogen pressure developed by electrolysis have been reported but information on the subject is incomplete (258, 260, 303, 378, 626, 670, 795, 919, 939).

Both the thickness and the surface conditions of metal specimens are factors affecting the permeability rate (303, 404, 527, 694, 697, 778, 795, 928, 939, 1024, 1076, 1154). The permeability is also influenced by the previous treatment of the metal. Iron previously subjected to hydrogen penetration is more readily permeable on each subsequent exposure. The increased permeability of freshly pickled iron is an example of this effect (173, 795, 939, 968). The iron may be restored to the initial permeability by a reconditioning heat treatment (173, 282, 554, 661, 684, 795, 902).

2.3. Solubility

According to the Hume-Rothery size-factor theory neither compounds nor solid solution will appear to any appreciable extent in the hydrogen-iron system (1137). The solubility of hydrogen in alpha iron is negligible at normal temperatures. The hydrogen solubility becomes measurable at about 400°C and increases linearly with increasing temperature to the alpha-gamma transformation temperature (A₃). The solubility increases abruptly at the A₃ point and continues increasing linearly. The effect of the gamma-delta (A₄) transformation on the solubility is controversial, some observers report a sharp decrease in solubility, others and more recent investigators report no effect at the A₄ point (95, 138, 139, 143, 442, 453, 481, 482, 513, 546A, 624, 682, 755, 791, 828, 850, 859, 973, 1010).

The possibility that the physical condition of the iron may influence the solubility of hydrogen has been suggested (155, 1060). The effect of size, shape, and condition of the metal on the hydrogen solubility data obtained has not been satisfactorily established (755, 828, 859, 1010).

2.4. Evolution and Removal of Hydrogen

It is generally assumed that the removal of hydrogen from solid iron is accomplished by heating, preferably at reduced pressure. However, the process is complicated by the effect of impurities in the iron and the varying rate of hydrogen evolution at different temperatures (1124). Mechanical working accelerates the evolution of hydrogen (28, 70, 237, 423, 440, 454, 463A, 594, 1007, 1030, 1150, 1152). The complete removal of hydrogen from solid iron is extremely difficult (655).

The evolution of hydrogen from iron varies irregularly with temperature, showing maxima and minima which tend to shift with composition (46, 68, 273, 300, 381, 442, 481, 647,
3. Effect of Hydrogen on the Properties of Iron

3.1. Structure, Physical and Mechanical Properties

Structure. Apparently there is no positive evidence that the microstructure of iron is affected by hydrogen (982), although the suggestion has been made that hydrogen, like silicon, develops conditions favorable to the formation of Neumann bands (1030A, 1150). Recrystallization may be influenced by hydrogen (298, 351, 368, 617). Interdendritic porosity (970, 1007, 1031, 1143, 1150, 1153) and large grain size (643, 1083) have been attributed to hydrogen. Hydrogen has been reported to increase the lattice constant of iron (368, 773) and to have no effect on the lattice constant (586, 1005), the latter being generally accepted.

Physical Properties. There is some evidence that temperature of the gamma-alpha transformation in iron is lowered by hydrogen (462, 485, 708, 747, 859, 973, 1174). The majority of investigators agree that hydrogen does influence the transformations in iron (2, 53, 68, 381, 462, 485, 570, 592, 708) although a few (105, 261) assert hydrogen has no effect.

The magnetic properties of annealed and unannealed electrolytic iron differ markedly (647). The abnormal magnetic hardness of cathodic iron was formerly ascribed to hydrogen (28, 35, 46, 128, 143, 257, 308, 416, 423, 1025, 1072) but structural factors, such as crystal size and residual stresses, are now generally considered the cause (474, 502, 609, 615, 616, 662, 668, 790, 861, 1006). Direct hydrogenation of iron apparently does not affect the hardness (528, 577, 1154), although an effect has been reported (978). It is generally agreed that hydrogen embrittles iron and its alloys as evidenced by a marked decrease in elongation (27, 30, 81, 237, 577, 584, 790, 983, 1030, 1047, 1076, 1152). Cold work increases the embrittling effect of hydrogen (1150). Cathode iron embrittled by hydrogen must be heated above the recrystallization temperature to completely remove the effect of hydrogen (303, 594, 970). This does not mean that all of the hydrogen has been removed.

3.2. Chemical Properties

Hydrogenation is reported to increase the susceptibility to chemical attack (55, 72, 137, 173, 764, 968, 1153). The solution pressure of iron is greater than that of hydrogen in aqueous solution. Overvoltage disappears at 96°C (175); however, at constant temperature below 96°C overvoltage increases with increasing current density (288, 473). Overvoltage is not affected by pressure changes (437). Absorbed hydrogen influences the chemical potential of electrolytic iron (558). Iron passivated in chromic acid is activated by the introduction of hydrogen into the passive iron (137, 764, 942, 968). One theory of passivity is based on the belief that it is not the result of an oxide film but of the absence or presence of absorbed hydrogen in the metal lattice (119, 134, 137, 968). It has been postulated that cathodic hydrogen enters the lattice and is dissociated into electrons and protons. Entrance of the electron into the third band transforms the iron from the passive to the active state (792, 797, 896, 923, 1075). Other theories are that escaping hydrogen reduces (1076) or fractures (1047) the protective oxide film. There are also theories of passivity which do not involve hydrogen. A review of the literature indicates there is not sufficient experimental evidence
to satisfactorily establish the mechanism of the phenomenon of passivity (1138).

The use of controlled atmospheres in industrial heat treatment and decarburization operations has supplied some information on the effect of hydrogen on specific impurities. It has been established that the effectiveness of hydrogen in removing carbon from steel is influenced by the amount of moisture in the hydrogen (283, 397, 524, 593, 1020). Failure to realize that moisture is a factor in decarburization may account for the divergent conclusions of early investigators as to whether hydrogen does (11, 19, 32, 57) or does not (81, 103, 116, 150) remove carbon from iron-carbon alloys. Subsequent investigations established the decarburization of iron-carbon alloys by hydrogen and have supplied much information on the effect of water vapor on the reaction (213, 258, 283, 321, 324, 358, 367, 394, 397, 416, 420, 459, 593, 694, 697, 747, 754, 760, 761, 806, 808, 829, 935, 1020, 1142).

Oxygen apparently is readily removed from iron by hydrogen treatment although a higher temperature is required than for the removal of carbon (31, 108, 312, 647). The moisture content of the hydrogen is an important factor in the reaction, and the oxygen removal is more effective if the iron is in the form of fine aggregate or is molten. (1020). Although deoxidation of iron by hydrogen occurs best at elevated temperatures, there is evidence, as indicated by microscopic examination, that cathodically charged hydrogen will attack some oxides under certain conditions of stress but analytical data to substantiate this observation are lacking (317).

Apparently it has been established that treatment with hydrogen at high temperatures also removes nitrogen (16, 18, 480, 498, 534, 549, 647, 702, 760), and may remove phosphorus (702) and sulphur (255, 317, 760).

A review of the literature on the hydrogenizing of iron indicates that the process may improve the magnetic properties of the metal, but the mechanism producing this result and the effect of variables noted in the preceding paragraphs have not been as satisfactorily established as is desirable. Discrepancies in results indicate that unknown variables other than temperature, the moisture content of the hydrogen, and chemical stability of non-metallic elements may be factors in the reactions.

4. Embrittlement Caused by Hydrogen from Different Sources

4.1. Hydrogen Absorbed by Molten Metal

An important source of hydrogen in steel is that inherited from the molten metal. Hydrogen is introduced in the steel furnace by: (1) the charge and addition agents (2) furnace gases. In either case the hydrogen is derived principally from water vapor which is reduced by the melt (6, 200, 246, 252, 253, 344, 539, 596, 597, 627, 651, 699, 749, 776, 777, 781, 813, 814, 842, 853, 862, 886, 904, 910, 931, 949, 960, 1014, 1028, 1030, 1031, 1032, 1036, 1059, 1061, 1068, 1130, 1139). Some hydrogen is present in the pig iron and scrap of the charge (218, 447, 536, 845, 853, 863, 931, 1053, 1069), light scrap carrying more hydrogen than heavy scrap and austenitic and alloy steels frequently carrying more hydrogen than simple steels (1162). Rusty scrap is recognized both as a means of introducing large amounts of hydrogen into the melt and as cause of flaking (81, 174, 194, 218, 749, 750, 863, 910, 920, 927, 961, 1028, 1053, 1069, 1079). Molten steel can pick up hydrogen from raw materials such as mill scale, ore and ferroalloys, slag materials such as lime, fluorspar and sand (166, 174, 218, 230, 447, 504, 536, 720, 749, 750, 805, 813, 840, 845, 863, 892, 910, 920, 927, 961, 1012, 1014, 1028, 1036, 1053, 1059, 1068, 1079, 1106, 1130, 1162). The effect of drying the lime charged into electric furnace heats was to reduce the hydrogen content of the metal from approximately 8 to 4 ml/100g, but no further decrease resulted from drying the ore (1162).

It is the general belief that a properly regulated carbon boil is the most effective means of removing excess hydrogen from the melt (234, 596, 694, 776, 781, 814, 815, 827, 842, 845, 853, 856, 886, 910, 949, 951, 966, 984, 1036, 1068, 1117); consequently, hydrogen introduced prior to the boil is without effect on the final hydrogen content (886, 910). The hydrogen content of a melt decreased from 5.1 ml before the boil to 3.7ml/100g after the boil, whereas in another heat the hydrogen content increased from 2.4 ml before the boil to 3.6ml/100g after the boil (1162). There is evidence from chemical analysis that a double boil increases the hydrogen content of the melt, and hydrogen defects have been observed in metal from
heats that have been given a double boil (1162); a prolonged refining period resulted in increased flaking (845).

The hydrogen in the melt seeks an equilibrium with the hydrogen in the furnace gases which blanket the melt (886, 910). Many fuels such as petroleum products and producer gas develop an environment rich in hydrogen (227, 251, 539, 597, 776, 813, 826, 904, 910, 920, 926, 949, 1014, 1036, 1046, 1059, 1061, 1069, 1130). The moisture content of the blast varies with atmospheric humidity (251, 904), and is usually higher in winter (776, 826, 1036).

The protective action of the slag is a variable factor in the absorption of hydrogen from the furnace atmosphere (845, 886, 908, 1012, 1080). Flaking in the solidified steel was found to be more frequent when the furnace slag was low in iron oxide and high in manganese (651, 691, 775, 776, 853, 912, 1069). Acid slags appear to give better protection against hydrogen absorption than do basic slags (650, 691, 706, 855, 886, 910, 927, 946, 961, 1059, 1135). Chemical analyses of solidified metal from acid and basic open hearth heats appear to substantiate this difference in hydrogen content (1155). The hydrogen content of solidified metal from acid open hearth heats is usually slightly less than that of metal produced by the normal electric-furnace practice, using lime (1162).

Improper alloying technique such as addition of wet ferroalloys after the boil or in the ladle may cause increases in hydrogen content (749, 845, 886, 892, 905, 910, 927, 1014, 1019, 1036, 1068, 1069, 1112, 1130, 1155, 1162).

The accuracy of hydrogen analyses of molten steel is questionable (1155), although an accuracy of ±0.5 ml/100g has been claimed for the pencil test (1162). In addition to the lack of accuracy in analytical methods, the method of sampling the molten steel may be a cause of inaccuracy. The hydrogen values reported for molten steel frequently were based on the hydrogen contents of the solidified metal, and such values are not necessarily satisfactory measures of the hydrogen content of the liquid metals (867, 894, 918, 992, 1000, 1023). These sampling and analytical difficulties have also handicapped investigation of possible hydrogen segregation during solidification of steel.

The hydrogen contents of solidified ferritic steels prepared according to normal commercial practice, vary from 3 to 8 ml/100g although hydrogen contents above 10 ml/100 g have been reported in wild heats, and austenitic steels may contain as much as 16 ml/100g (1155, 1162). In experiments on a laboratory scale, hydrogen contents of 4.0 to 7.0 ml/100g were obtained from solidified steels that had been treated by passing hydrogen through the molten steel, then quenched from the casting temperature. Addition of titanium, zirconium, and columbium increased the amount of hydrogen retained. Hydrogen-treated melts of 18Cr—8Ni steel contained as much as 17.5 ml of hydrogen per 100g (905).

The effect of alloying elements or impurities on the amount of hydrogen retained in the solidified steel obviously is a combination of the effects on the solubility of hydrogen in the molten metal, the amount of hydrogen evolved during solidification, and the solubility of hydrogen in the solid metal. The solubility of hydrogen in molten steel is difficult to determine directly, and the amount of hydrogen evolved during solidification and that retained in solid steel is affected by other factors, for example, the conditions and rates of cooling. Consequently, interpretation of analyses made on the solidified metal, in terms of conditions that may have existed during solidification or in the molten state, is difficult and the results may be misleading and contradictory. For example, an increase in silicon in the charge increased the hydrogen content of cast iron (1161) but silicon retarded the evolution of hydrogen during solidification of iron silicon alloys (905). Hence, if silicon increases the amount of hydrogen retained in solid iron-silicon alloys, and at the same time lowers the solubility of hydrogen in the solid metal, the increase can only represent supersaturation resulting from an unknown combination of solubility in the liquid metal, solidification phenomena, and rate of cooling during and after solidification.

Further examples of the uncertain and contradictory nature of the effect of alloying elements on the hydrogen content include the agreement of several authors (71, 147, 155, 205, 229, 539, 892, 988) that silicon, manganese, nickel, chromium, carbon, tungsten, titanium, and columbium increase, and molybdenum and vanadium decrease the hydrogen remaining in the solid metal, whereas recent work in England (1155, 1162) fails to substantiate these conclusions. More thorough investigation of the behavior of hydrogen during solidification of steel to correlate such factors as hydrogen retention, hydrogen evolution during solidification, hydrogen and the effects of alloying elements on these factors is needed.

Information on the influence of other gases on hydrogen in steel is confined largely to the
physical removal of hydrogen by gases (536, 802, 1129A). Deoxidizers, such as aluminum, silicon and manganese, reduce the amount of carbon monoxide formed and thus decrease the hydrogen removed by the washing action of the carbon monoxide (77, 155, 322, 338). Iron nitride is reported to retain hydrogen (486).

An example of the practical significance of the rate of evolution of gas during solidification of the metal is the widely investigated phenomenon of the formation of skin holes in rimmed steel. Some investigators ascribe this to hydrogen (14, 24, 33, 34, 38, 39, 46, 64, 86, 88, 168, 197, 235, 252, 306, 328, 364, 365, 413, 495, 497, 515, 536, 539, 561, 567, 651, 654, 776, 803, 857, 887, 949, 1101), others absolve hydrogen from blame (7, 12, 47, 48, 79, 102, 112, 113, 124, 141, 142, 157, 180, 186, 190, 200, 231, 331, 369, 374A, 430, 507, 533, 565, 568, 654, 848, 857, 862, 876, 893, 992, 1055, 1119, 1121). Other phenomena such as flakes, shattercracks, hairlinecracks, etc., attributed to hydrogen, undoubtedly are affected by the amount of hydrogen introduced in the molten metal, but, because these phenomena are encountered in steel after it has solidified, they will be discussed in the next section.

The importance of factors controlling the solubility and retention of hydrogen is obvious but there is a dearth of information on the subject. Extensive investigation is needed to correlate the hydrogen content of molten metal, the solidification reactions, and residual hydrogen with the effect of cooling rates, alloy content, alloying technique and ingot mass.

4.2. Hydrogen Absorbed or Retained by Solid Steel

Hydrogen may be absorbed in solid metal by exposing the metal in a hydrogen environment at elevated temperatures or as a result of chemical and electrochemical action where-in hydrogen is released at the liquid-metal interface.

Hydrogen retained in the solid metal is that portion of the hydrogen which dissolved in the liquid metal and was not eliminated during the solidification or subsequent cooling from solidification temperatures, plus hydrogen absorbed by the solid metal. The effects attributed to the hydrogen existing in solid steel are in general embrittling effects under various titles.

The apparent embrittlement of steel by hydrogen was noted at the turn of the century (81). Work on single crystals of iron indicated that hydrogen decreases cohesion across the cubic cleavage plane (366). The elongation and reduction in area values of freshly rolled open-hearth steel were improved by aging and by a low-temperature anneal (200° to 600°C), the improvement being attributed to loss of hydrogen (666, 707). The yield point, elongation and reduction in area of a steel were lowered when the steel was melted in an atmosphere containing hydrogen (654); a similar effect was observed when hydrogen was introduced by heating solid metal in hydrogen (1160). Other observer (1162) reported that ductility was reduced by the hydrogen retained on solidification in excess of a critical amount; the reduction in area was affected more seriously than the elongation, and the ductility in the transverse and radial directions was affected more than in the longitudinal direction.

Presence of small amounts of hydrogen in the atmosphere of an annealing furnace has been reported to cause embrittlement (950, 1157). Steel wire heated in hydrogen was embrittled, as demonstrated by bend and torsion tests, whereas similar treatment in nitrogen did not produce a similar reduction in properties (594).

The amount of hydrogen retained in solid steel and the effect on the properties varied with the composition and condition of the steel, and with such factors as the teeming practice, the rate of solidification and contact of the molten metal with moisture in runners and moulds, (101, 120, 122, 132, 217, 413, 444, 508, 532, 536, 594, 654, 664, 666, 751, 904, 905, 910, 927, 929, 937, 950, 959, 960, 973, 990, 1028, 1030, 1061, 1112, 1124, 1155, 1160, 1162). Sensitivity to hydrogen embrittlement increases with increase in the carbon content (576, 591, 654, 699, 751, 927, 951, 959). Elements which form stable carbides are said to suppress the deleterious effects of hydrogen (927, 1160). It is reported that chromium (1012) and manganese (1076) increase retention, whereas nickel up to 4 percent exerts no influence (1012); however, the steels whose properties are most affected by hydrogen are nickel-chromium, nickel-chromium-molybdenum and chromium-molybdenum steels (1124).

The term “flake” is often used in a broad sense in the literature to include various types of defects attributed to hydrogen and observed in the fracture or microstructure. These defects were first observed in steels produced commercially; they have been purposely produced by the introduction of hydrogen into the steel. Treatment of the steel with nitro-
gen under otherwise identical conditions failed to develop flakes (643, 664, 674, 707, 713, 769, 785, 970, 974), and conversely, the removal of hydrogen decreased the tendency to flaking, i.e., slow cooling of steel is an accepted method for preventing flake formation (226, 325, 403, 465, 560, 583, 532, 643, 650, 651, 658, 664, 674, 681, 700, 701, 706, 707, 713, 714, 715, 719, 724, 726, 727, 728, 732, 736, 737, 738, 740, 741, 742, 743, 750, 769, 772, 776, 780, 785, 827, 830, 849, 866, 908, 944, 961, 1009, 1033, 1053, 1124, 1150). Also, flakes in steel may be removed or prevented by hot forging or rolling accompanied by proper heat treatment to remove hydrogen (214, 325, 403, 465, 560, 583, 591, 595, 611, 873, 1058) although the foregoing operation has been questioned as ineffective in removing flakes (595) and as unnecessary (174, 610).

Observations have been made that forging (599, 610, 650, 664, 719), melting practice (162, 225, 264), pouring practice (48, 225) humidity and climatic conditions (184, 681) and alpha-gamma relationships (595, 706, 714, 719, 776, 780, 833, 855, 974, 1098) affect the sensitivity of steel to flaking.

Variation of the tendency to flaking with composition (403, 426, 706, 719, 970, 973, 974, 1098, 1011, 1174, 1162) is similar to the effect of composition on hydrogen retention and evolution. Variations in flaking tendency were observed in different heats of the same composition (1098) and in different ingots of the same heat (1042). It has been reported that the combination of stresses and metallographic structure resulting from a certain cooling procedure may make the steel susceptible to a specific type of hydrogen defect described as “fisheyes” (1162).

The tendency to develop flakes is effected by alloy constituents, such as nickel, chromium and molybdenum although critical percentages of individual constituents were not determined (183, 403, 426, 678, 719, 905, 974, 1011, 1058, 1098, 1124). There is some evidence that the composition of the steel controls the critical concentration of hydrogen necessary to cause flaking (908, 974, 977, 1124). Satisfactory correlation of the relationship is hampered by lack of information on the effect of other variables, i.e., recent observations indicate that metallographic structure also may be a factor in determining this critical hydrogen concentration (1160, 1162).

The manifestation of hydrogen embrittlement where macrocracks are produced has received consideration by investigators in England where the defects are termed “hairline cracks.” Early investigators associated hairline cracks with flakes (218, 276, 320, 325, 362, 403, 961) and the development of explanations of hairline crack formation parallels that on flaking (211, 218, 245, 275, 276, 320, 401, 403, 451, 631, 691, 728, 736, 854).

The outstanding research on hairline cracks is that sponsored by the Hairline Crack Committee of the British Iron and Steel Institute. In planning the investigation it was evidently assumed that hairline cracks were attributable either to hydrogen or to stress systems within the metal, or to both. The published reports indicate the experimental work has been concentrated on hydrogen to the exclusion of other possible causes (654, 885).

The only method developed so far for the laboratory production of hairline cracks is by introduction of thermal hydrogen into the steel (974, 1124). A sufficient concentration of hydrogen in the metal will produce hairline cracks even in the absence of allotropic transformations or cooling stresses, and stresses resulting from allotropic transformations do not produce hairline cracks in the absence of a critical hydrogen content (1124). In commercial steel production an incubation period, i.e., a lapse of time between cooling and hairline crack formation, has been observed (451, 720, 721, 729, 780, 877) and this incubation period has been observed also in the production of hairline cracks in laboratory investigations (974). Hydrogen evolution from hydrogen-treated steels showed a similar incubation period, which varied with the composition of the steel (905, 974, 1124, 1133, 1134). Reheating within the incubation period eliminated crack formation; without reheating, the number of cracks increased with increase in the hydrogen concentration (1013).

Steel exposed to hydrogen at temperatures below the Ar1 or steels exposed to hydrogen above the Ar1 and then cooled below the Ar1 prior to quenching are not susceptible to hairline cracks (726, 974, 1124). Susceptibility to the formation of hairline cracks increases with depression of the gamma-alpha transformation (885, 1124). Hydrogen is reported to retard the gamma-alpha transformation at high temperatures but to produce a slight accelerating effect when the transformation occurs at low temperature. Susceptibility to the formation of hairline cracks is not related to the quantity of hydrogen lost during allotropic transformation but is related to the temperature range of maximum evolution; a wide temperature range of hydrogen evolution is coupled with low susceptibility to hairline cracking (1013, 1124). The investigations
were too limited in scope to establish the effect of alloy content or other variables on the evolution of hydrogen from steel.

It is inferred that there is a difference in the susceptibility for the formation of hairline cracks in cast and forged metal of the same composition (1162). Cracking does not always result from high hydrogen content (1124, 1162). The difficulty in correlating hydrogen content and susceptibility to cracking is seen in the freedom from cracks in specimens of highly stressed ball-bearing steel having higher hydrogen content than similar steels which develop cracks despite lower stress and lower hydrogen content. Similarly, hydrogen treated Jominy bars failed to crack in the quenched end but displayed many cracks in the slow-cooled end; tyre steel cracked in the hard end but not in the soft end; in manganese steels cracks were formed in both ends. Other bars, such as 2 to 3 per cent nickel, cracked in segregated areas separated by sound areas (1124). A study of the hydrogen contents of a series of steels representing different stages of manufacture (1162) confirms the many experiments carried out in steel which have been artificially impregnated with hydrogen (1160) and indicates that the ductility is reduced with hydrogen contents in excess of 2ml/100 g. The opinion (1162) is expressed that while macrostresses bring out in a very clear manner the embrittling effect of hydrogen, the appearance of hairline cracks in material which has been slowly cooled and is, therefore, free from major stresses of this type, is attributable to the combined effect of hydrogen, local stresses, and poor ductility in some preferred direction.

The term “shattercrack” was applied principally to defects in rail steel which produce transverse fissures (149, 160, 209, 222, 272, 325, 555, 636, 645, 646, 651, 673, 716, 721, 769, 866, 915, 926, 945, 1091). Shattercracks have been produced artificially in rail steel by treatment of the melt with hydrogen (769, 785, 927, 945, 990). The temperature ranges in which they form vary with the composition of the steel and are about the same as the temperatures which produce flakes (716, 724, 866, 874, 889, 900, 903, 926, 945, 1052). Application of slow cooling cycles was developed by the rail industry prior to association of hydrogen with the formation of shatter cracks (160, 163, 184, 186A, 193, 425, 443, 555, 579, 644, 666, 745, 926).

The development of the opinion that hydrogen is associated with shatter crack formation parallels the development of the same opinion on the formation of flakes and hairline cracks (119, 127, 163, 174, 186A, 201, 236, 250, 555, 644, 679, 715, 721, 724, 818, 873, 926, 945, 1009). The investigations of shatter cracks in rails furnish little basic information on the hydrogen-steel system. The work is of interest as an empirical development of the recommended procedure for the removal of hydrogen from steel prior to the association of hydrogen as a possible cause of shattercracks.

It is generally agreed that, retained hydrogen can exist in steel in two forms: atomic and molecular. Atomic hydrogen is presumed to exist in the lattice whereas molecular hydrogen is present in voids in the steel. Though it has been suggested that the molecular form does not affect the properties of the steel (267), it is more generally believed that the molecular hydrogen in voids is under pressure and that the pressure exerted by the molecular hydrogen is responsible for cracks and embrittlement (927, 969, 970, 1031, 1150). The belief that hydrides form in steel is unsubstantiated (652). The proposed theories of hydrogen retension in steel fail to explain data obtained experimentally or to predict the behavior of hydrogen-treated steel with respect to embrittlement (1124).

Studies of the effect of retained hydrogen in steel throw little light on the mechanism of embrittlement. Steels with different concentrations of hydrogen may or may not flake, depending upon other factors such as, internal stresses, composition, etc. (1124, 1160, 1162).

The quantity of hydrogen retained on thermal charging is limited to the solubility in solid steel and the retention curve falls below the solubility curve with increasing temperature (594, 947, 1115). The data on retention has been obtained principally on small specimens so the mass was relatively insignificant. The effect of increasing mass on retention has not been determined despite the fact that it is large masses, not small that are important industrially.

Rate of cooling appears to exert more influence on retention of hydrogen than does the chemical composition of the iron and steel, although more thorough investigation might alter this observation (1124, 1162).

Hydrogen is much more soluble in austenite than in ferrite and is rejected from the lattice during the gamma to alpha transformation (1083). When gamma and alpha iron co-exist, hydrogen is assumed to concentrate in the gamma phase (1124). It has been suggested that the expulsion of hydrogen from traces of austenite which transform last may explain the formation of hairline cracks. No one has succeeded in producing hairline cracks in austenitic steels (1162). However,
the rapidity with which hydrogen diffuses, and the occurrence of an incubation period preceding the formation of hairline cracks throw doubt on a simple hydrogen pressure or hydrogen embrittlement theory (1162).

Steel specimens heated in hydrogen show 20 to 30 percent less expansion in transforming from gamma to alpha than similar specimens heated in nitrogen (1160). A possible explanation of this difference is the expansion of the gamma lattice by hydrogen (1124), but no such increase in the volume of gamma iron was observed during hydrogen treatment (1160).

In recent work there has been considerable interest in the diffusion of hydrogen within the steel (974, 1160, 1162). Abnormalities in hydrogen diffusion were observed, particularly below 300°C (1162) and preferred paths of diffusion may be a partial explanation of the abnormalities (1150). Apparently the metallographic structure and carbide formation are among the factors influencing diffusion and solubility. Stresses have been suggested as another factor (1160). The evolution of hydrogen at room temperature is associated with formation of hairline cracks (974, 1160, 1162). Relatively high concentrations of hydrogen may be retained in austenitic steels without any indication of evolution of hydrogen resulting from cooling (905, 1124). Such steels are reported free of flaking (1098, 1162), indicating that evolution of hydrogen is dependent upon the occurrence of an allotropic transformation (885, 905, 1124, 1160). The rate of evolution is a function of the rate of an allotropic transformation (1160). It has been suggested that the cracking of steel in a brittle manner results from prestressing by tessellated stresses which are in turn caused both by hydrogen and cooling (1016). The reduction in area and the transverse properties are most affected. Consequently steel high in hydrogen is subject to failure under systems of triaxial stresses (1162). Micro-cracks, macro-cracks and flakes are associated with large grain size (516, 601, 973, 1058, 1098).

Satisfactory evaluation of the effect of the numerous variables which may affect the retention of hydrogen in steel is impossible from a study of the investigations thus far reviewed. The evidence presented shows that there are many variables which affect hydrogen embrittlement. The generally accepted theory that cracks are propagated in steel by the combination of residual stresses and the pressure of hydrogen accumulating in the voids is without direct experimental proof. The theory fails to explain many of the observed peculiarities of hydrogen in steel, such as, incubation period, described in section IV-2. The hydrogen pressure theory was first proposed about 50 years ago. The present theory (970, 1124), is a rewording of the original theory to adapt it to the mosaic void theory of metallic structure.

Establishment of a mechanism of embrittlement, flaking, and cracking in steel has been handicapped by lack of adequate basic data on the iron-hydrogen system, as shown in section 2 of this review. Experimentation has defined the conditions under which certain defects occur in laboratory specimens, but proof that the results are generally applicable to commercial practice is lacking. In industry it is necessary to treat each problem separately and arrive at an empirical solution.

Even in laboratory investigations the experimental difficulties involved in controlling the numerous variables have resulted in a mass of conflicting data. Most investigations of hydrogen-induced defects have utilized chemical or thermal methods for introducing hydrogen into the solid steels, whereas the difficulties experienced in commercial practice are largely the result of hydrogen retained by the metal during solidification. Proof is lacking that thermally introduced hydrogen and hydrogen retained during solidification produce the same degree of hydrogen embrittlement. Nevertheless, most investigations of hydrogen-attributed defects have proceeded on the assumption that conclusions based on the embrittlement of hydrogen obtained from one source are valid for all conditions of hydrogen contamination. The effect of alloying elements on hydrogen embrittlement may be associated as much with condition and structure of the steel as with changes in hydrogen solubility.

The ratio of hydrogen retained in cooling to the loss occurring on standing has been claimed to be important, but there have been very few investigations giving data that correlate values for this ratio with condition, structure, composition, and similar variables. There is also a lack of data correlating the foregoing ratio with hydrogen embrittlement.

Difficulties inherent in the accurate determination of the hydrogen content of steel have added to the confusion on hydrogen embrittlement. In addition, there are also the difficulties of sampling resulting from the fugacity and the possible segregation of hydrogen.

There is evidence indicating that occluded hydrogen may be retained in slip and cleavage planes, suggesting the possibility of preferred paths of diffusion. Retention of hydrogen by a semichemical binding might ac-
count for irregularities in evolving hydrogen. Adsorption of hydrogen in certain crystallographic planes has been suggested. Fresh surfaces show relatively high adsorption, and steel subject to hydrogen defects is usually characterized by allotropic transformation whereby such surfaces are formed. More information on the hydrogen absorbed in the solid state might aid in understanding the mechanism of hydrogen embrittlement of steel.

4.3. Hydrogen Absorbed in Chemical Reaction

The earliest observations on the penetration and embrittlement of iron by hydrogen were made with hydrogen originating from chemical or electrochemical reactions (3, 5, 8, 26, 30, 31, 37, 50, 55, 61). This phase of hydrogen embrittlement is of particular importance in connection with the cleaning of metals by chemical action.

Hydrogen evolution at the liquid-metal interface is considered necessary for absorption of hydrogen (220, 872, 939) although this has been questioned (919). Hydrogen embrittlement may occur where any chemical reaction results in the release of nascent hydrogen, and the release of nascent hydrogen is not confined to acid solutions (97, 153, 202, 206, 254, 293, 798, 851, 963, 1077). Embrittlement is a frequent result of cathodic or acid cleaning (3, 5, 26, 30, 31, 110, 161, 173, 206, 220, 260, 274, 378, 450, 594, 693, 751, 795, 928, 940, 956, 963, 1008, 1022, 1027, 1077, 1078, 1084, 1088, 1154), and is influenced by the type of electrolyte and the conditions of the operation (161, 173, 594, 956, 978, 1027).

In early investigations the quantity of hydrogen liberated electrochemically was correlated with the voltage and current density (99, 173, 260, 378, 692, 928). However, when embrittlement is used as an indication of electrochemical absorption a threshold effect is exhibited, that is, embrittlement does not occur until the current density exceeds a specific minimum value (378, 684, 693, 795, 928, 939, 956, 1027, 1154), which is influenced by the composition and physical condition of the steel (1027, 1150, 1151). The simultaneous application of electrolysis and tensile stress to steel increases the hydrogen embrittlement effect, which reaches a maximum when the stress is at the yield point (317).

In the commercial chemical cleaning of steel it is claimed that either the use of an oxidizing acid or anodic cleaning will avoid embrittlement (237, 542, 732, 795, 928, 939, 956, 1027, 1077, 1078, 1084). However, anodic cleaning has been blamed for embrittlement (161, 450), although it is reported to occur only above critical values of voltage and current density (956).

Increase in acid concentration of pickling baths, within limits, increases the rate of attack (173, 268, 361, 693, 1113, 1126), but increase in temperature is still more effective in accelerating the pickling action (50, 303, 924, 928, 1126, 1150). The pickling action is related to the release of total nascent hydrogen, but the latter is not necessarily related to the absorption of hydrogen and, therefore, to embrittlement (795, 939).

The effects of bath temperature on the absorption of nascent hydrogen are controversial, some claiming that variations of 10 to 20°C have little effect on the rate of absorption (940, 1022) whereas the contrary is claimed by others (237, 303, 361, 924, 1150). Some investigators report a continued increase in absorption of cathodic hydrogen with increase in bath temperature from 0°C to 100°C (924, 1150), others report critical temperatures between 0°C and 100°C at which the absorption rate reaches a maximum and does not increase further with increase in temperature (237, 303, 367). As much as thirty-fold increase in the rate of absorption of nascent hydrogen into steel with increase from room temperature to 80°C has been reported (928).

The composition of the electrolyte has an important influence on the rate of absorption of hydrogen (303, 405, 527, 641, 693, 817, 928, 1027, 1126). Time is also a factor, the absorption of hydrogen being most rapid in the initial stages although threshold effects influence the results (303, 361, 378, 405, 527, 641, 684, 693, 795, 817, 940, 956, 978, 1021, 1022, 1027, 1176, 1154). Other factors include thickness of specimens (594, 630, 940, 1022), composition of steel, (161, 237, 450, 542, 612, 755, 959, 1088, 1115, 1153) condition, and microstructure (1150). With few exceptions, the conclusions reached have been based on physical tests and not on actual chemical analysis for hydrogen.

The amount of hydrogen evolved from an electrolytic cell usually increases with increase in temperature hence a smaller proportion of hydrogen is absorbed by the metal as the temperature is raised (405, 817). The composition of the electrolyte also affects the ratio between evolved and absorbed hydrogen. Hence, evolved hydrogen is not useful as a measure of hydrogen absorbed in the metal unless all conditions are indentical.

The degree of embrittlement resulting from electrolytic charging of steel with hydrogen may vary either with the impurities present in the electrolyte, in the steel or both. The
effect of impurities will vary with such factors as concentration and location, i.e., in the electrolyte or in the steel. Impurities appear to have more effect on hydrogen absorption in electrolysis than in acid pickling (1008, 1151).

Impurities in acid electrolytes, cited as promoters of hydrogen absorption, include iron (378, 1176), sodium sulphide (939, 1022), sulfur (303, 542, 638, 693, 757, 928, 1084, 1153), phosphorus (693, 757, 901, 928, 1084), bismuth (673, 928), antimony (693, 928), tellurium (542, 693, 928), arsenic (464, 612, 693, 757, 901, 928, 1153, 1154), hydrogen sulfide (526, 638, 693, 817, 928, 1154), mercury (646, 693, 928, 1154), copper (221, 361), silver (221), platinum (221, 757), lead (693, 928), zinc (693, 757, 928), cadmium (693, 928), selenium (542, 693, 757, 928, 1153), tin (757), and carbon bisulfide (542). The effect of impurities in caustic electrolytes has not been investigated as extensively, but mercury (346, 464, 612) and arsenic (464, 542) have been listed as promoters of hydrogen absorption.

The action of promoters differs with respect to method, that is, chemical or electrochemical cleaning, and for the solution used (346, 361, 464, 542, 693, 928, 1126, 1153, 1154). The presence of two or more promoters in solution may modify the action of one, for example, arsenic acts as an inhibitor in the presence of hydrogen sulfide. Colloidal sulfur produces a large increase in the absorption of hydrogen but addition of mercury salts blocks this effect (542). Failure to recognize the effect of electrolytic impurities may account for some of the discrepancies in the data pertaining to embrittlement by chemical cleaning.

While inhibitors are used in commercial pickling primarily to prevent loss of metal by acid attack, they may aid in controlling hydrogen embrittlement (148, 210, 248, 361, 450, 582, 640, 732, 733, 787, 901, 1078, 1126, 1131, 1151, 1154). Inorganic inhibitors include iron, arsenic, antimony, phosphates, silicates and chromates (42, 72, 73, 148, 173, 221, 361, 529, 580, 582, 600, 639, 704, 734, 888, 901, 1018, 1126, 1154). Salts of metals which have a comparatively high overvoltage give an inhibiting action by plating out on the surface of the iron or steel (472, 585, 734, 880, 1131).

There is a lack of information on the effect of variation in conditions on the action of inhibitors and accelerators. Results obtained under closely controlled laboratory conditions may not be valid for conditions obtained in commercial practice. Similar uncertainties are present in the field of organic inhibitors (37, 99, 260, 268, 290, 396, 406, 456, 458, 517, 582, 613, 628, 718, 730, 731, 734, 1126, 1131, 1156).

There is ample evidence that the surface condition of steel is an important factor in the absorption of hydrogen, especially in chemical cleaning processes (173, 303, 670, 684, 693, 758, 795, 901, 928, 939, 940, 1008, 1022, 1150). Etching, oxidation and abrasion increase the absorption of hydrogen by steel (173, 303, 684, 693, 755, 758, 928, 1008) whereas polishing renders the metal less susceptible to hydrogen embrittlement (693, 928, 940, 1022). However, the effect of polishing varies with the technique employed (633, 1003, 1017, 1114), perhaps because of variation in the amount of cold-work produced. Cold-work influences hydrogen penetration of steel although satisfactory quantitative data on the effect of cold-work are not available.

The effect that surface condition has on absorption of hydrogen is influenced by the method in which the nascent hydrogen is produced (684, 693, 758, 795, 928, 1008). Surface layers may receive an initial charge of hydrogen during acid pickling, which blocks further flow of hydrogen (940, 978, 1022). This phenomenon is a possible factor in embrittlement by chemical processes but the information available is not conclusive.

Recent evidence that susceptibility to hydrogen embrittlement is influenced by both heat treatment and composition (1150) throws doubt on much of the previous work which ignored the possible effect of these factors. Many investigations indicate that cold work affects the susceptibility to embrittlement and the rate of diffusion (237, 450, 594, 978, 1022, 1027, 1150, 1154), but more recent work indicates that, although the sensitivity of steels susceptible to embrittlement is increased by cold-work, steels not susceptible to embrittlement are not affected by cold-work (1150). Hardened steel is more sensitive to embrittlement than cold-drawn (1027). Chemical attack varies with cold-work and crystal orientation (871). The wide divergence in the results reported on the effect of cold-work indicates that other unrecognized factors may also exert an influence.

Austenitic steels apparently are not susceptible to acid embrittlement (1154) and martensitic steels are especially susceptible to embrittlement (1150). The condition of the carbon in steel influences the diffusion of hydrogen (795). Lamellar pearlite retards diffusion whereas spheroidal cementite facilitates diffusion (405, 455, 594, 928, 940, 1022).
In view of the number of variables which affect embrittlement of steel by nascent hydrogen the common practice of using the degree of embrittlement, as determined by physical tests, as a measure of the extent of hydrogen penetration appears inaccurate.

Gas, other than hydrogen, in steel usually increases the hardness (795). Investigation has shown that hydrogen usually does not harden the steel (787, 812, 1154), although a slight increase in hardness has been reported to result from electrolysis (978), but not from pickling. The ductility of steel is lowered by the presence of hydrogen, as indicated by decreases in the elongation and reduction in area (26, 31, 161, 237, 360, 441, 450, 582, 588, 594, 640, 783, 970, 978, 1027, 1077, 1153). The ability of steel to withstand bending is decreased by the presence of hydrogen (519, 1077, 1153) and the bend test has been used as a test for pickling embrittlement (1154). The tensile strength is reported both to be decreased by hydrogen (26, 31, 64, 1027, 1077), and to be increased (582, 783, 943, 1027). The tensile strength of steel is raised by electrolysis but lowered by pickling (978).

A much greater variation in properties results from embrittlement with nascent hydrogen than from embrittlement with thermal hydrogen. This difference has been ascribed to the notch effect resulting from nonuniform penetration of hydrogen during electrolysis (1160). Exposure of steel to nascent hydrogen is reported to alter the notched bar impact values (748) although others observed no such effect (441, 450). Edge cracks and checks in rolled sheets have been attributed to hydrogen (757, 943, 970, 979, 1027, 1077, 1153) also pickling blisters (37, 405, 450, 594, 734, 751, 795, 970). Pickling embrittlement is said to increase the susceptibility of steels to acid attack (970, 1153). The passivity of stainless steel may be destroyed by hydrogen (1002).

The loss in ductility as a result of pickling embrittlement is reduced by aging at room temperature or at elevated temperature, and the recovery is correlated with evolution of hydrogen. However, permanent damage may result from hydrogen contents above critical values (542, 737, 751, 978, 1022); below a critical degree of embrittlement no permanent damage is observed (940, 1022).

The evolution of hydrogen from steel is a function of time and temperature (542, 594, 940, 1022, 1089), whereas the retained hydrogen is the important factor in embrittlement (864, 1154). Loss of hydrogen from steel subjected to pickling or electrolysis is apparently little affected by oxidizing conditions such as anodic treatment or immersion in nitric acid (1154). Tempered wire recovers from embrittlement more rapidly than cold worked wire (1027). Humidity (1022) and the method of introducing nascent hydrogen (978, 1089) are other variables that complicate the study of embrittlement by nascent hydrogen.

In general, the data accumulated from studies of the embrittlement by pickling or electrolysis indicate that hydrogen is the cause of embrittlement. However, the lack of knowledge of the effect of the many variables discussed in this review and the difficulty in controlling these variables have resulted in considerable discordance in the data produced and disagreement in the conclusions drawn therefrom. It cannot be said that a mechanism of embrittlement by nascent hydrogen has been satisfactorily established.

5. Summary

A survey of the literature has shown that hydrogen embrittlement of steel has been the subject of extensive investigation, but the data and conclusions are in considerable disagreement. Much of the contradictory data and disagreement in conclusions results from the number of variables that affect hydrogen phenomena in steel and the difficulty in recognizing and controlling these variables. Another factor contributing to the contradictory and disagreements is the deficiency of data for correlating hydrogen in iron to hydrogen in steel. The lack of reliable values for hydrogen content, does not permit the determination of the efficiency of procedures used to introduce or remove hydrogen in steel. The absence of a uniform nomenclature also contributes to the confusion.

There is considerable circumstantial and some factual evidence relating the embrittle-
ment of steel to hydrogen but proof is lacking that hydrogen is the sole cause of all the service failures ascribed to it. Favorable points for the hydrogen theory are that flakes, hairline cracks, pickling embrittlement, and similar defects have been duplicated in the laboratory by the use of hydrogen, and that procedures which cause the removal of hydrogen from steel also reduce the occurrence of such defects. However, many of the defects attributed to hydrogen have been explained also on the basis of other causes.

It would appear that the available knowledge of hydrogen embrittlement can be summarized in the statement: If all the prescribed procedures for maintaining the hydrogen content at a minimum are utilized, certain undesirable effects generally ascribed to hydrogen can be lessened or eliminated.

6. Selected Bibliography

1800–1900

1. Annable, W., Iron 22, 348 (1883).
7. Callietet, L., Compt. rend. 56, 847 (1863); 58, 327–328, 1037 (1864); 60, 344–345 (1865); 61, 899–892 (1865); 64, 1067 (1867); 66, 847–850 (1868); 80, 319–321 (1875); 80, 847–490 (1875).
141. Stead, J. E., J. Iron Steel Inst. (London) 83, 54-71 (1911); 85, 104-113 (1912).
156. Bosch, Z. Elektrochem. 24, 261 (1918).
473. Gladstone, S., "The Electrochemistry of Solutions" (1929).
472. Dunn, T. E., U. S. Pat. 1,775,671 Sept. 16 (1930).

460. "Vacuum Melting for Quality; why not?" Metals Tech. (AIME) TP268 (1930).

528. Cioffi, P. P., Bell Lab. Record 10, 159-163 (1932);
530. Clarke, A. K., J. Am. Chem. Soc. 54, 1885-1899
1016. Laszlo, F., J. Iron Steel Inst. (London) 147, 196 (1943); 149, 758 (1944).
1943
1042. Cathcart, D., Metal Treatment 11, 112 (1944).
1038. Alexander, J. J., Blast Furnace Steel Plant 32(3) 346-351, 1213-1219 (1944); Iron Steel Engr. 21, 2341-2344 (1944).
1161. Somers, E. V., and Gunther, D. W., Foundry 75(3) 66–69, 218, 220, 222, 224, 226, 228 (1947).
1161. Somers, E. V., and Gunther, D. W., Foundry 75(3) 66–69, 218, 220, 222, 224, 226, 228 (1947).
1161. Somers, E. V., and Gunther, D. W., Foundry 75(3) 66–69, 218, 220, 222, 224, 226, 228 (1947).
1161. Somers, E. V., and Gunther, D. W., Foundry 75(3) 66–69, 218, 220, 222, 224, 226, 228 (1947).
Solders and Soldering

Soldering is one of the easiest and most satisfactory methods of joining metals that can be used with equal success by both the handyman and the professional. The three classes of solders treated in this publication are soft solders, precious metal solders, and common brazing solders. The selections of fluxes, which can be as important as the choice of solder, is adequately discussed.

All common soldering alloys are listed, and their component elements, together with their melting ranges, are given. Illustrations of different types of soldered joints are shown, and types of soldering equipment are described and illustrated.


Mechanical Properties of Metals and Alloys

Contained in this comprehensive book is a summary of technical literature on ferrous and nonferrous metals and alloys, including data on strength and related properties, thermal expansion, and thermal and electrical conductivities at normal, high, and low temperatures.

Information on aluminum, copper, iron and steel, lead, magnesium, nickel, tin, zinc, a number of miscellaneous metals, and their alloys are included. In general, data are presented in tabular form, although graphical representation is used to indicate the effects of changing composition or conditions on the mechanical properties.
